1970

Diffusion and internal friction in sodium-rubidium silicate glasses

Gary L. McVay

DIFFUSION AND INTERNAL FRICTION IN SODIUM - RUBIDIUM SILICATE GLASSES

by

GARY LEE McVAY, 1943-

A DISSERTATION

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI - ROLLA

In Partial Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

in

CERAMIC ENGINEERING

1970

D. E. Day
Advisor

Warren Haby

H. P. Hughes

Robert M. Dell

R. C. Moore

ABSTRACT

The internal friction and self diffusion coefficients of sodium and rubidium ions for (1 - X) $Na_2O \cdot X\ Rb_2O \cdot 3\ SiO_2$ glasses have been measured. The diffusion measurements employed radioactive isotopes and a thin sectioning technique and extended from 350 to 500°C. Internal friction measurements were made from -150 to 500°C and at frequencies of 0.05 to 6000 Hz. The maximum height for the mixed alkali internal friction peak occurs at the composition where the sodium and rubidium diffusion coefficients are equal. It is concluded that the mechanism responsible for the mixed alkali peak is a cooperative rearrangement of sodium-rubidium ions and that the slowest moving ion controls the rate of this rearrangement. This mechanism should also apply to other mixed alkali silicate glasses since the internal friction for these systems is similar.

The height of the alkali peak was compared with the corresponding alkali ion diffusion coefficient for several alkali aluminosilicate and silicate glasses. A direct correlation was found between the height of an alkali peak and the magnitude of the diffusion coefficient of the appropriate alkali ion.

ACKNOWLEDGEMENT

The author gratefully acknowledges the aid and advice given by Dr. Delbert E. Day, major advisor. Appreciation is also expressed for the helpful discussions with Dr. Norbert J. Kreidl and Dr. Manfred Wuttig.

The financial support provided by the NSF and NASA Traineeships was very much appreciated.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (continued)

LIST OF TABLES

I. INTRODUCTION

Internal friction measurements, as a function of temperature, for single alkali silicate glasses show two peaks which are referred to as the alkali and non-bridging oxygen peaks.[1-4] When a glass contains a mixture of dissimilar alkali ions, an unusually large internal friction (or mechanical damping) maximum is observed as first reported by Rotger[5] and Jagdt[6]. They suggested that mixing the alkalis caused the original alkali peak to become larger and move to higher temperatures. By making small additions of a second alkali, Steinkamp, Shelby, and Day[7] found that the large peak previously reported was actually a new peak. Since the new peak was observed only in mixed alkali glasses they referred to it as a "mixed alkali peak."

Shelby[8] and de Waal[9] recently investigated the mechanical damping of mixed alkali silicate glasses. The second alkali in some of de Waal's glasses was introduced by ion-exchange, but the internal friction of these glasses was similar to that for comparable glasses prepared by conventional melting. They both attributed the large internal friction peak to an interaction between dissimilar alkali ions. The magnitude and activation energy for the mixed alkali peak was reported by Shelby to depend upon the radius ratio of the alkali ions. Shelby and de Waal both proposed a position interchange of dissimilar alkali ions as the mechanism for the mixed alkali peak. Shelby reasoned that if the larger ion was in a region of compression and the smaller ion was in a region of tension when a stress was applied, then an exchange of position would reduce the total stress. In a more general sense a pair of dissimilar alkali ions might be considered to form an elastic

dipole. With the application of a stress, therefore, these dipoles change position so as to reduce the total stress.

The preceding model implies that the rearrangement of dissimilar alkali ions should occur most readily when the ions move at about the same rate. Since the diffusion coefficient serves as a measure of ion movement, a correlation would be expected between the magnitude of the mixed alkali internal friction peak and the diffusion coefficients for the different alkali ions in various glass compositions.

This study was undertaken to investigate in greater detail the mechanism previously proposed for the mixed alkali internal friction peak; i.e., a mutually cooperative rearrangement of dissimilar alkali ions. Unfortunately, the diffusion coefficients of both alkali ions, for any glass system in which the internal friction has been measured, are not available. Therefore, alkali ion diffusion coefficients and internal friction were measured systematically for the glasses $(1 - X)\ Na_2O \cdot X\ Rb_2O \cdot 3\ SiO_2$. Radioactive tracers and a thin-sectioning technique were used to determine the self diffusion coefficients of the sodium and rubidium ions. The internal friction was measured using a torsion pendulum and a resonance technique based on Forster's[10] method.

II. EXPERIMENTAL PROCEDURE

A. Glass Preparation

The glasses listed in Table I were prepared from reagent grade Na_2CO_3, Rb_2CO_3 and potter's flint (99.98% SiO_2). All the glasses were melted in platinum crucibles in an electric furnace open to the atmosphere. After melting at 1550°C for several hours with periodic stirrings, the bubble-free glass was poured into rectangular bars using stainless steel molds. Glass fibers approximately 0.5 mm in diameter were also pulled from the same melt. The bars and fibers were annealed at the temperatures shown in Table I. See Appendix A for more details.

B. Diffusion Measurements

Sodium and rubidium self diffusion measurements were made by a thin-sectioning technique, illustrated in Appendix C, Figure 17, using the radioactive isotopes Na^{22} and Rb^{86}. The diffusion coefficients reported are the average of two samples processed simultaneously. Initially, the annealed rectangular bar was cut into samples approximately 1/8" thick. After polishing the ends of the samples, the desired isotope was evaporated onto one end in a vacuum evaporator. The plated samples were heat treated in air in an electric resistance furnace controlled to $\pm 1/2$°C. Heat treatments were in the temperature range 350-500°C for times from 1/2 to 24 hours. Portions of the edges of each sample were removed to reduce any effects of surface diffusion.

Each sample was mounted to a sectioning apparatus similar to that described by Williams[11], by using a high temperature wax. This apparatus utilizes abrasive paper for sectioning and allows the sample to be removed for weighing, while assuring that all sections are

TABLE I

Compositions and Heat Treatment Temperatures

Glass No.	Molar Composition			Heat Treatment Temperature (°C)	Density (gm/cm^3)
	Na_2O	Rb_2O	SiO_2		
I*	1.00	0.00	3.00	515	2.446
II	0.98	0.02	"	515	
III	0.95	0.05	"	510	
IV*	0.75	0.25	"	510	2.617
V*	0.50	0.50	"	505	2.769
VI	0.37	0.63	"	515	
VII*	0.25	0.75	"	530	2.901
VIII	0.10	0.90	"	565	
IX*	0.00	1.00	"	580	2.966

*Diffusion measurements were made on these glasses

parallel. Section thicknesses varied from 2-15 microns and the total thickness removed was 100-200 microns. The thickness of each section was calculated from the density of the glass, the cross-sectional area of the sample, and the weight of each removed section. After sectioning, the specimen was wiped with a small piece of lint-free paper to remove any loose particles adhering to the glass; this paper was folded inside the abrasive paper. A fresh piece of abrasive paper was used for each section. The activity of each section was determined by placing the folded abrasive paper in the well of a scintillation counter. The diffusion observed in this study is described by the equation:

$$Ai = (Ao/\sqrt{\pi Dt}) \exp(-Xi^2/4Dt) \quad (1)$$

Ai = Activity concentration at distance Xi from the surface

Xi = Distance from the sample-isotope interface

t = Time of diffusion

Ao = Original activity at Xi=0, t=0

D = Diffusion coefficient

The diffusion coefficients determined in this study compare favorably with those in the literature, Table II.

C. Internal Friction Measurements

The internal friction was measured from -140 to 500°C using an inverted torsion pendulum and a resonance technique often referred to as the Forster[10] method. All measurements were made at a vacuum of less than 10^{-2} torr. At a heating rate of 1.5°C/min, the temperature gradient over the length of the samples never exceeded 3°C in the pendulum and 5°C in the resonance apparatus. The internal friction was calculated from the following equation:

TABLE II

Comparison of Measured Diffusion Coefficients
With Those Found in the Literature

Glass	$D_{Na}(\frac{Cm^2}{sec})$ at 415°C	
	Literature	Present Technique
16 $Na_2O \cdot 12CaO \cdot 72\ SiO_2$	8.7×10^{-10} (11)	9.1×10^{-10}
25 $Na_2O \cdot 75\ SiO_2$	9.5×10^{-9} (18)	1.2×10^{-8}

$$Q^{-1} = \frac{1}{n\pi} \ln (\text{Amplitude ratio})^* \qquad (2)$$

Q^{-1} = Internal friction

n = Number of cycles

Amplitude ratio = Ratio of the amplitude of periodic specimen motion on the zeroth cycle and the n^{th} cycle

*This can also be the velocity ratio

A diagram of the torsion pendulum, which operated over a frequency range of 0.05 to 1.00 Hz, is shown in Appendix B, Figure 10. Samples used in the pendulum were fibers approximately 50 mm long and 0.5 mm in diameter. The temperature was measured by three Chromel-Alumel thermocouples, located along the length of the glass fiber.

The resonance apparatus, Appendix B, Figure 11, operated over a frequency range of 1500 to 6000 Hz. Samples used in this apparatus were rectangular bars approximately 1/4" x 1/2" x 4-6". The bars were suspended horizontally from two loops of fused silica thread located close to the vibrational nodes. Temperatures were determined by three Chromel-Alumel thermocouples embedded in a glass bar of the same dimensions as the specimen and located adjacent to the specimen.

D. Activation Energy - Internal Friction

The apparent activation energy of the mixed alkali peak, using both internal friction techniques, was calculated from the equation:

$$Ea = R \left(\frac{\ln f_1 - \ln f_2}{1/T_2 - 1/T_1}\right) \qquad (3)$$

Ea = Activation energy

f_1 & f_2 = Frequency for a maximum of the internal friction peak

T_1 & T_2 = Temperature (^oK) of the internal friction peak for frequencies f_1 and f_2 respectively.

While measurements at only two frequencies are necessary to calculate the activation energy, four to seven frequencies between 0.08 and 5000 Hz were used. The error in the activation energy is considered less than $\pm$ 1 kcal/mole. Using both internal friction techniques allows the activation energy to be determined more accurately than by using either technique alone.

III. RESULTS

A. Diffusion

In the temperature range 350-500°C, the diffusion coefficients for sodium and rubidium ions were found to fit the normal Arrhenius equation:

$$D = D_o \exp(-E/RT) \quad (4)$$

D = Diffusion coefficient

D_o = Pre-exponential factor

E = Activation energy

R = Universal gas constant

T = Temperature, °K

The self diffusion coefficients, activation energies, and pre-exponential factors for sodium and rubidium diffusion are given in Tables III and IV.

Typical plots of log D versus 1/T are shown in Figure 1. The lines in the lower part of the figure are for rubidium diffusion while those in the upper part are for sodium diffusion.

The variation of the sodium and rubidium diffusion coefficients with composition, between 350 and 500°C, is illustrated in Figure 2. Portions of the curves have been omitted for clarity. As the fraction of rubidium ions increases, the diffusion coefficient for rubidium increases while that for sodium decreases. It should be noted that at each temperature the curves intersect at practically the same composition, Rb/(Rb+Na)=0.73.

B. Internal Friction

Internal friction curves for the Na - Rb silicate glasses are illustrated in Figure 3. For the glass containing only sodium, X = 0.00, the first peak at -32°C corresponds to the alkali peak while that at

TABLE III

Self Diffusion Coefficients, Activation Energies, and Pre-exponential Factors for Sodium Diffusion

Glass No.	D_{Na} cm^2/sec				E (±1) kcal/mole	Do cm^2sec
	350°C	400°C	450°C	500°C		
I	2.95×10^{-9}	9.50×10^{-9}	2.55×10^{-8}	6.10×10^{-8}	19.5	2.10×10^{-2}
IV	3.00×10^{-10}	1.57×10^{-9}	6.30×10^{-9}	2.15×10^{-8}	27.4	1.31
V	5.10×10^{-11}	3.10×10^{-10}	1.45×10^{-9}	5.60×10^{-9}	30.2	2.23
VII	1.47×10^{-11}	1.03×10^{-10}	5.60×10^{-10}	2.45×10^{-9}	32.6	4.45
IX	5.00×10^{-12}	3.85×10^{-11}	2.25×10^{-10}	1.08×10^{-9}	34.4	6.15

TABLE IV

Self Diffusion Coefficients, Activation Energies, and Pre-exponential Factors for Rubidium Diffusion

Glass No.	D_{Rb} cm^2/sec				E(±1)	Do
	350°C	400°C	450°C	500°C	kcal/mole	cm^2/sec
I	9.50×10^{-13}	5.45×10^{-12}	2.40×10^{-11}	9.20×10^{-11}	29.4	2.01×10^{-2}
IV	1.18×10^{-12}	1.12×10^{-11}	7.90×10^{-11}	4.30×10^{-10}	38.0	2.71×10^{1}
V	3.50×10^{-12}	3.10×10^{-11}	2.05×10^{-10}	1.10×10^{-9}	36.9	3.24×10^{1}
VII	1.80×10^{-11}	1.24×10^{-10}	6.40×10^{-10}	2.80×10^{-9}	32.4	4.34
IX	1.38×10^{-10}	6.00×10^{-10}	2.08×10^{-9}	6.20×10^{-9}	24.4	5.31×10^{-2}

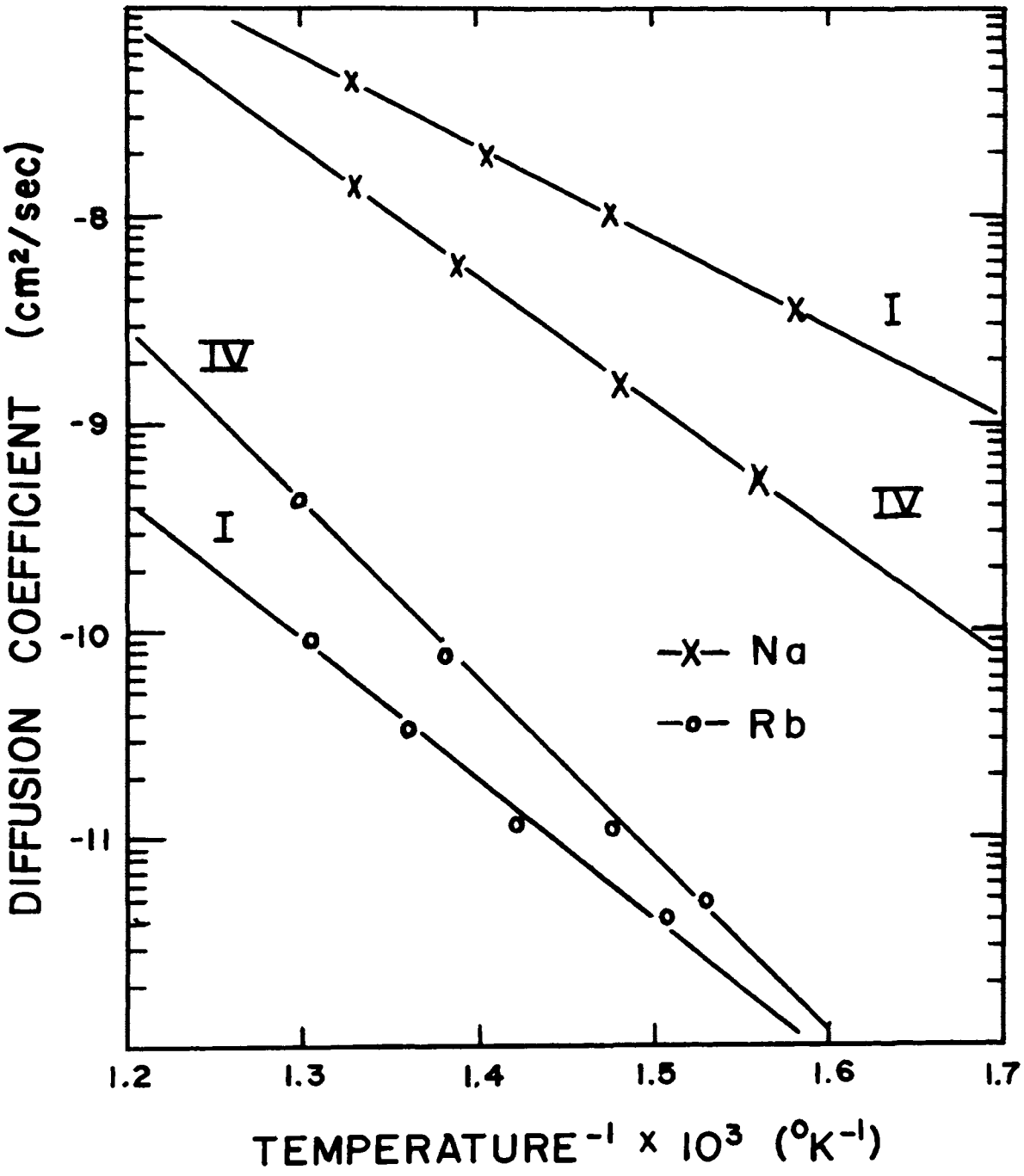

Figure 1. Temperature Dependence of Sodium and Rubidium Diffusion Coefficients for Glasses I and IV

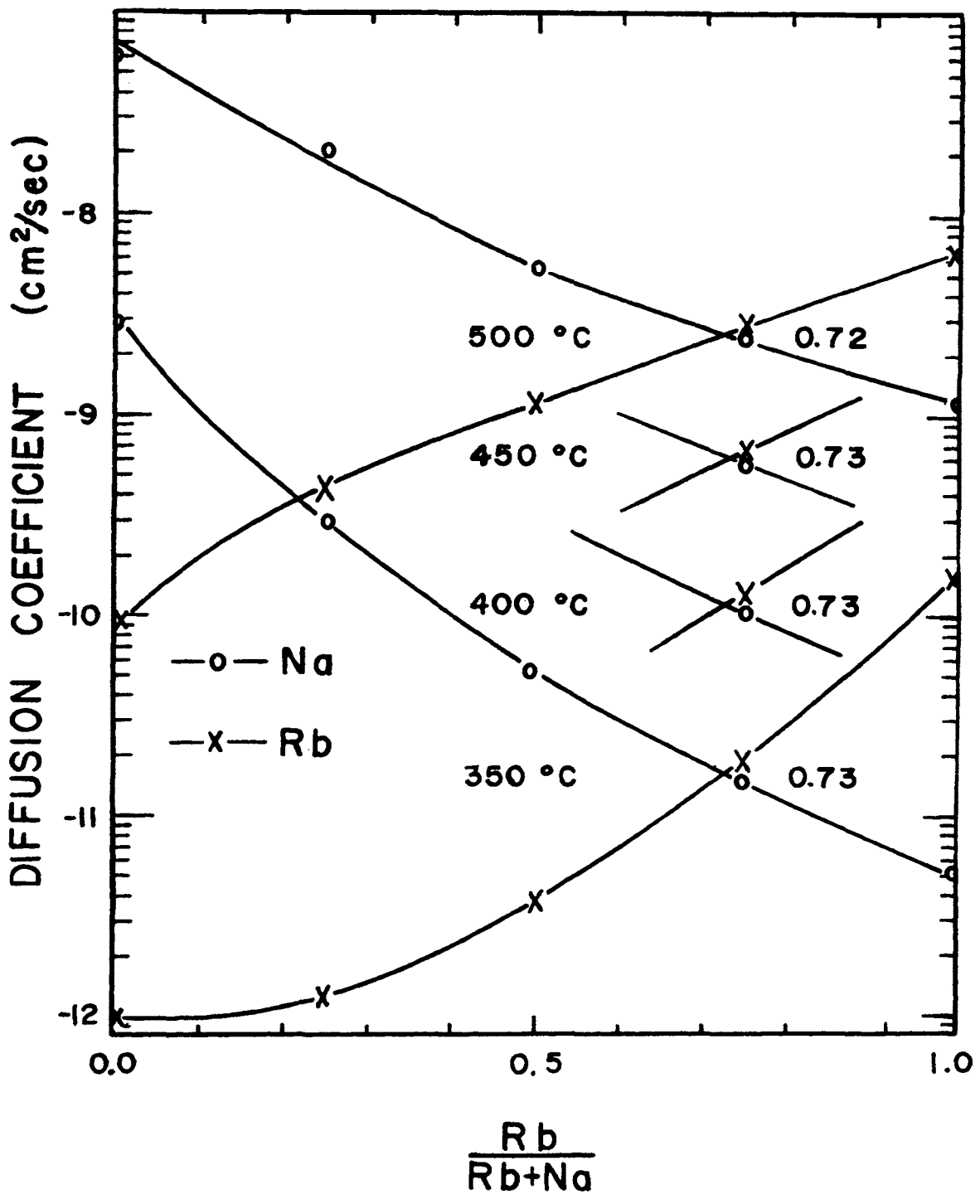

Figure 2. Self Diffusion Coefficients for Sodium and Rubidium in (1 - X) $Na_2O \cdot X\ Rb_2O \cdot 3\ SiO_2$ Glasses

182°C is the non-bridging oxygen peak. With the addition of rubidium the mixed alkali peak initially appears in the vicinity of the non-bridging oxygen peak, but at higher temperatures, and rapidly grows in magnitude.

Changes due to composition in the mixed alkali peak temperature and height above background are shown in Figure 4. The peak temperature goes through a broad minimum while the peak height reaches a maximum at a Rb/(Rb + Na) ratio of 0.70. Within experimental error, this is the same composition at which the curves for the diffusion coefficients of sodium and rubidium intersect, Figure 2.

C. Activation Energy

Figure 5 shows how the activation energy for alkali diffusion and the mixed alkali peak change with composition. The activation energy for the mixed alkali peak changes only slightly, about 4 kcal/mole. The activation energy for both sodium and rubidium diffusion, however, changes about 14 kcal/mole. Note also that the activation energy for sodium and rubidium diffusion are equal at a Rb/(Rb + Na) ratio of 0.74.

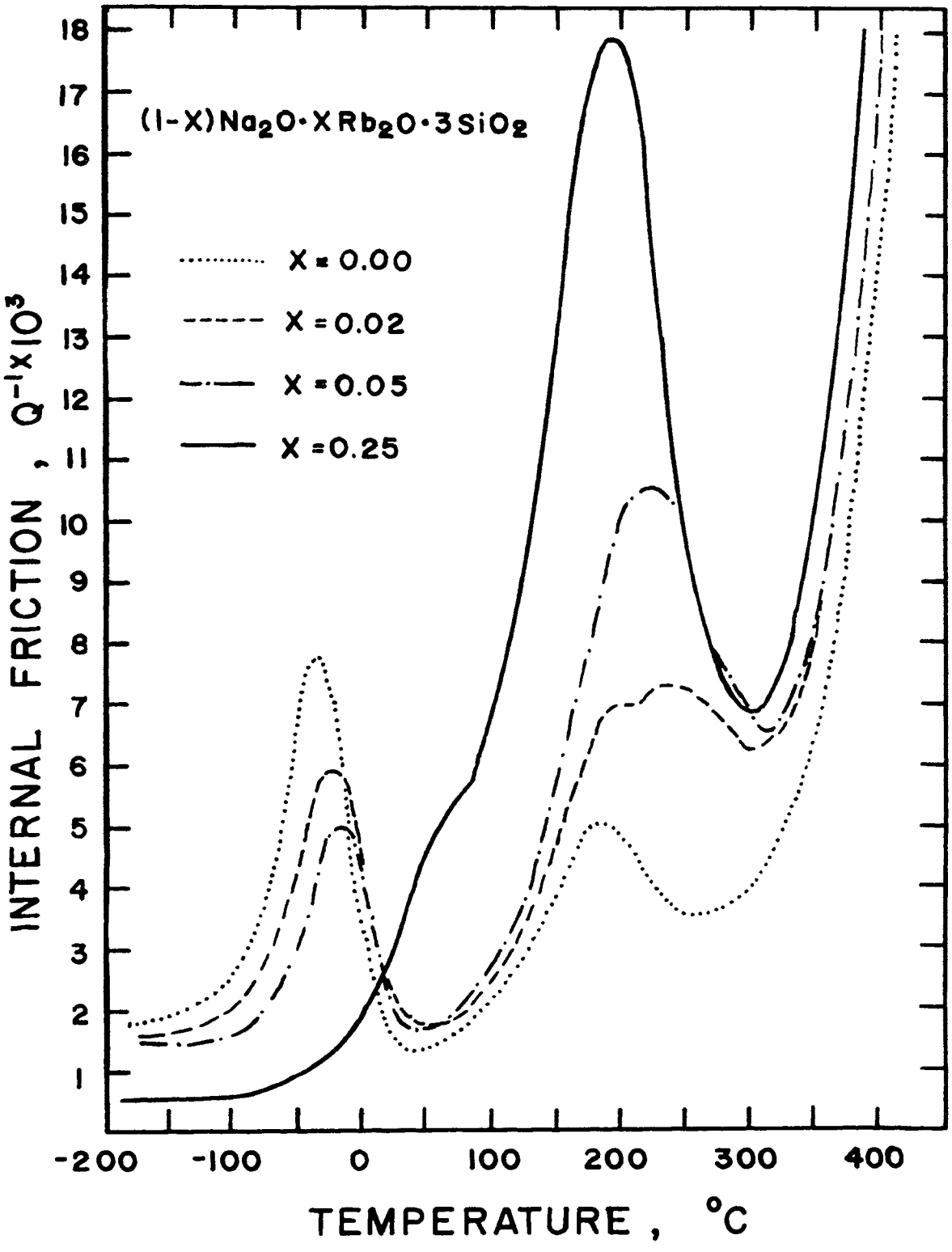

Figure 3. Internal Friction Curves for the (1 - X) $Na_2O \cdot X\ Rb_2O \cdot 3\ SiO_2$ Glasses, Freq. = 0.4 Hz

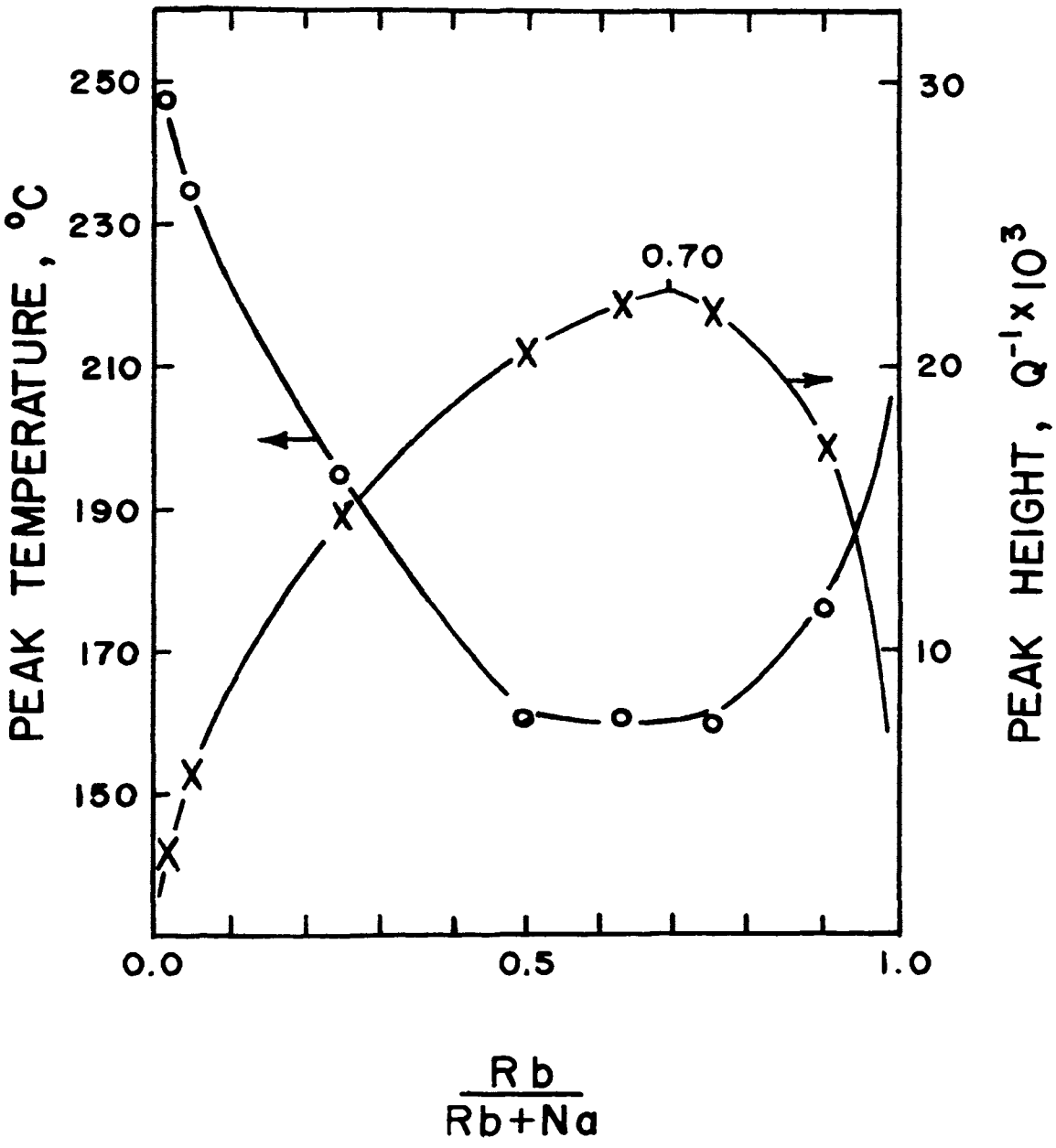

Figure 4. Temperature and Height Above Background for the Mixed Alkali Peak in (1 - X) $Na_2O \cdot X\ Rb_2O \cdot 3\ SiO_2$ Glasses, Freq. = 0.4 Hz

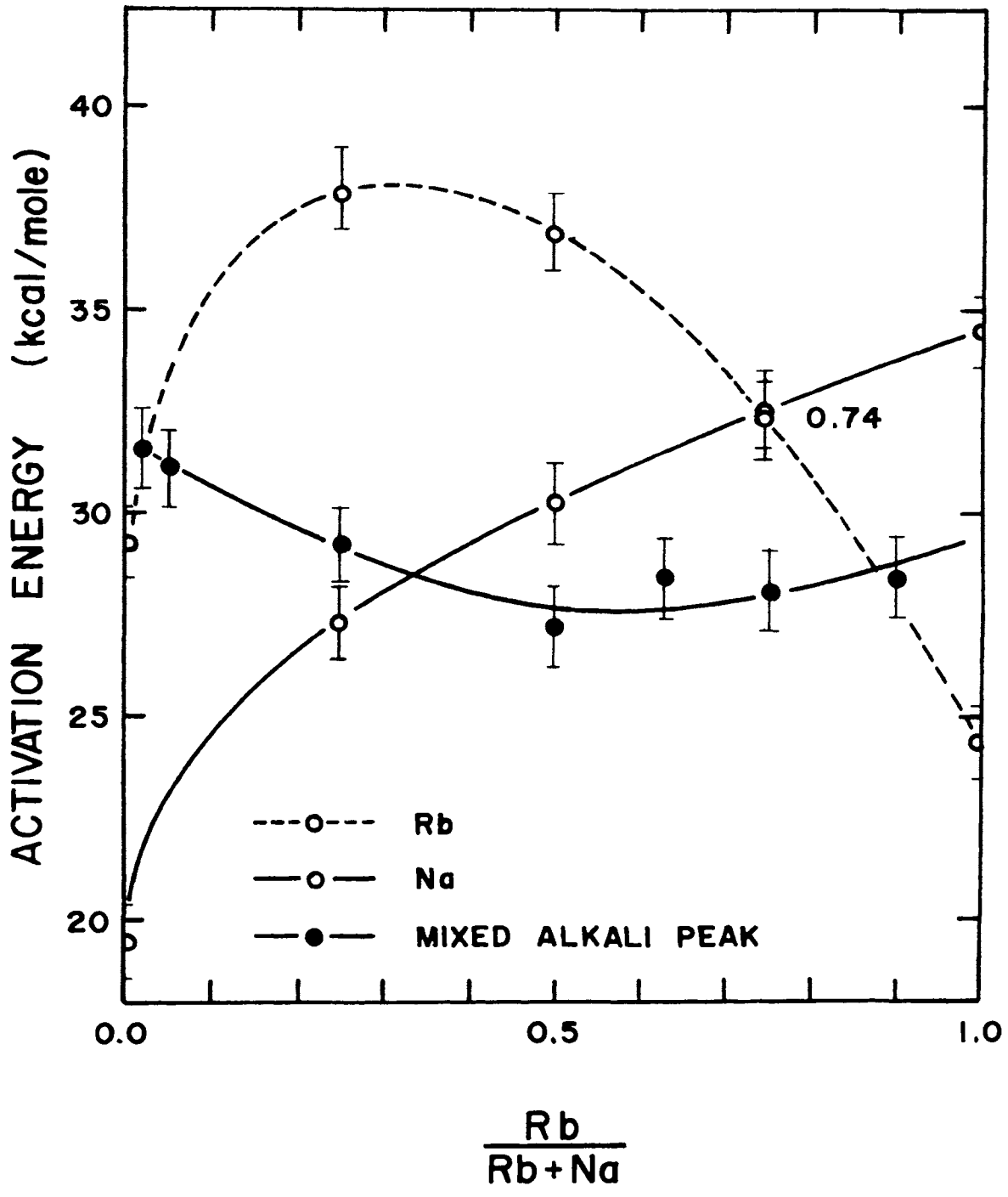

Figure 5. Activation Energy for Alkali Diffusion and the Mixed Alkali Internal Friction Peak in (1 - X) $Na_2O \cdot X\ Rb_2O \cdot 3\ SiO_2$ Glasses

IV. DISCUSSION

A. Comparison of Activation Energies for Alkali Ion Diffusion with that for the Mixed Alkali Internal Friction Peak

There is no apparent correlation between the activation energy for the mixed alkali peak and that for either sodium or rubidium single ion diffusion, as shown by Figure 5. If the mixed alkali peak involved the movement of only a single alkali ion, then some correlation would be expected between the activation energy for the mixed alkali peak and that for single ion movement. Since this is not observed the mixed alkali peak is considered to involve the cooperative movement of both alkali ions, as previously proposed.

A cooperative rearrangement mechanism has also been suggested for certain internal friction peaks in various metals. An internal friction peak found in substitutional alloys such as α - Cu Zn, α -Ag Zn, and Cu Al is attributed to the stress-induced reorientation of solute atom pairs.[12] In other words, when a stress field is applied, the solute atom pair aligns itself with the resulting strain field in order to reduce the stress. No correlation has been observed between the activation energy for internal friction and that for the diffusion of either solute or solvent atoms in these substitutional alloys.[13]

B. Analysis of Mixed Alkali Peak

If the mixed alkali peak is assumed to involve the cooperative movement of a sodium and rubidium ion, as indicated by the lack of correlation between the activation energies, then one must account for the maximum peak height not occurring at a Rb/(Rb + Na) ratio of 0.50. On the basis of a purely statistical pairing, the proportion of sodium-rubidium pairs is given by 2 Nna (1-Nna) where Nna is the fraction of

sodium ions. The 2 is present because Na - Rb and Rb - Na pairs are considered indistinguishable. The concentration of pairs is a maximum, therefore, when the Rb/(Rb + Na) ratio equals 0.50. However, the maximum peak height shown in Figure 4 occurs at a Rb/(Rb + Na) ratio of 0.70. The Na - Rb system is not unique, as Shelby[8] found the maximum mixed alkali peak height for Li - Na, Na - K, and Li - K (75 mole % SiO_2) glasses to occur at ion ratios (concentration of larger alkali ion/total alkali concentration) of 0.55, 0.60, and 0.85 respectively. Similarly Steinkamp[14] found the maximum mixed alkali peak height for Li - Na aluminosilicate glasses at a Na/(Na + Li) ratio of 0.60, while de Waal[15] found the maximum at a Na/(Na + Li) ratio of 0.62 (67 mole % SiO_2). Thus, in all the systems studied the maximum height for the mixed alkali peak is not observed at that composition where the maximum number of dissimilar alkali ion pairs is expected.

In addition to the concentration of relaxing units, there are two other factors that can affect the peak height. First, a decrease in the distribution of relaxation times will increase the height, while an increase will reduce the height, all other factors remaining constant. If the distribution of relaxation times became smaller in the glasses containing from 0.50 to 0.80 moles Rb_2O, then this could account for the maximum peak height occurring at 0.70 moles Rb_2O. However, there is no evidence of any change in the distribution of relaxation times.

For a mechanism with a single relaxation time, the peak width at half-height is given by:[16]

$$\Delta \left(\frac{1}{T}\right) = 2.635 \frac{R}{Ea} \qquad (5)$$

$\Delta(\frac{1}{T})$ = Peak width at half-height, $^{o}K^{-1}$

R = Universal gas constant

Ea = Activation energy

Changes in the distribution of relaxation times resulting from composition changes can be determined by comparing the observed half-height peak width with that calculated from equation 5. This ratio, as seen in Table V, remains practically constant for the Na - Rb glasses. Shelby[8] also observed very little change in the distribution of relaxation times for similar Li - Na glasses. Thus, the maximum in peak height cannot be accounted for by a change in the distribution of relaxation times.

Another factor affecting peak height is the relaxation strength per relaxing unit. In other words, the energy absorbed by the reorientation of a sodium-rubidium pair. The relaxation strength might change with composition in such a way that the height of the mixed alkali peak would be larger even though the concentration of relaxing units had been decreased by compositional changes. Unfortunately, no method for quantitatively evaluating the relaxation strength has been devised. Hence, there is no basis for predicting how the relaxation strength might change with composition. For the time being it is assumed that the relaxation strength does not change significantly with composition. A similar assumption was made by Shelby[8] for other mixed alkali silicate glasses.

The only factor left for consideration is the concentration of relaxing units. Statistically, the largest proportion of sodium-rubidium pairs should occur when the Rb/(Rb + Na) ratio equals 0.50. Of interest, however, is the fraction of pairs able to participate in the relaxation process. Thus, the concentration of relaxing units

TABLE V

Distribution Parameters and Activation Energies for the Mixed Alkali Peak of Sodium-Rubidium Silicate Glasses

Glass No.	Peak Width ($\frac{1}{T} \times 10^3$) (± 0.04) Observed	Peak Width ($\frac{1}{T} \times 10^3$) (± 0.01) Calculated	$\frac{\text{Peak Width Obs.}}{\text{Peak Width Calc.}}$ (± 0.2)	Activation Energy (kcal/mole) (± 1 kcal/mole)
II	--	--	--	31.6
III	0.55	0.17	3.2	31.1
IV	0.58	0.18	3.2	29.3
V	0.66	0.19	3.4	27.2
VI	0.65	0.19	3.4	28.4
VII	0.67	0.19	3.5	28.1
VIII	0.57	0.19	3.2	28.4

should be defined in terms of the concentration of "active" pairs. If the two alkali ions move at considerably different rates, then a cooperative rearrangement of the ions should depend upon the slowest moving ion. While the total number of pairs in a particular glass may be large (in comparison to another composition) the concentration of relaxing units; i.e., the fraction of active pairs, may be relatively small if the diffusion coefficients of the alkali ions are greatly different. The composition containing the largest concentration of active pairs, therefore, should be that where the diffusion coefficients of the two alkalis are the same.

As shown in Figure 2, the diffusion curves for sodium and rubidium intersect at a Rb/(Rb + Na) ratio of 0.73. Within experimental error this is also the same composition where the peak height is a maximum Rb/(Rb + Na) = 0.70, Figure 4. Thus, while the proportion of sodium-rubidium pairs is largest at a Rb/(Rb + Na) ratio of 0.50, the fraction that is active (i.e., concentration of relaxing units) is less than that where Rb/(Rb + Na) = 0.73. The correlation between the composition where the alkali ion diffusion coefficients are the same and the composition corresponding to maximum height for the mixed alkali peak illustrates the dominating influence of the relative mobilities of the alkali ions. Furthermore, the concentration of relaxing units need not be directly related to the total concentration of ion pairs as calculated from composition.

The importance of the slowest moving ion to the mechanism proposed for the mixed peak is further illustrated in Figures 6 and 7. The cross-hatched region in Figure 6 shows the slowest moving ion for the Na - Rb glasses at 400°C. In crystalline materials, the diffusion

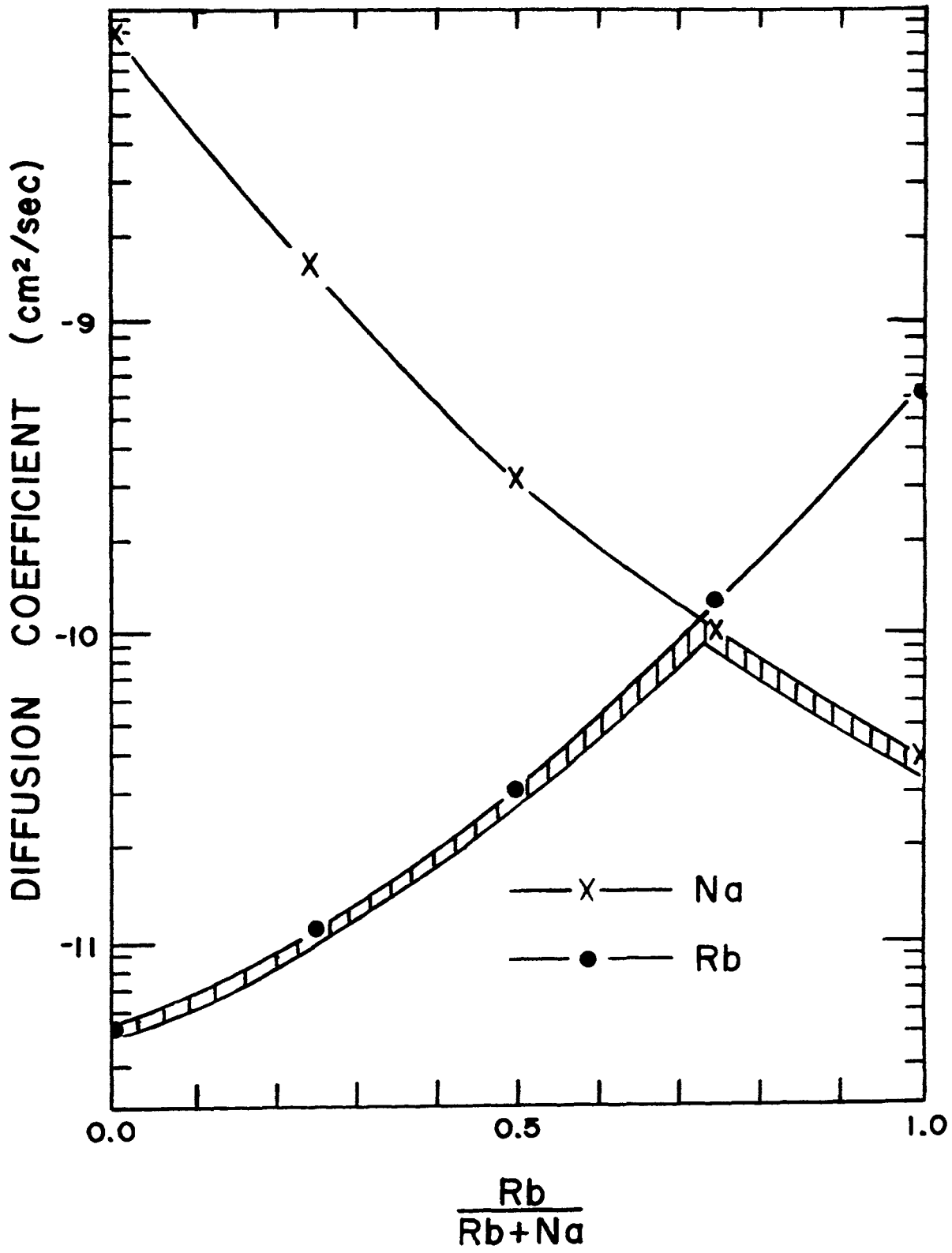

Figure 6. Path of the Slowest Moving Ion in (1 - X) $Na_2O \cdot X\ Rb_2O \cdot 3\ SiO_2$ Glasses, Temp. = 400°C

coefficient is related to the relaxation time for the appropriate internal friction peak by the equation:[17]

$$D = \frac{\alpha a^2}{\tau} \qquad (6)$$

D = Diffusion coefficient

a = Jump distance

α = Constant which depends on the structure

τ = Relaxation time

Since the two constants a and α are unknown for glasses, the equation is not directly applicable for determining the diffusion coefficient from internal friction measurements. However, this equation as applied to glasses shows that the diffusion coefficient and relaxation time are inversely proportional. If the slowest moving ion is the rate controlling factor for a cooperative rearrangement of a sodium-rubidium ion pair, then the relaxation time for the mixed peak should be a minimum at that composition where the slowest moving ion has the largest diffusion coefficient, i.e. at Rb/(Rb + Na) = 0.73. The relaxation time for the mixed peak as calculated for 200 and 300°C and shown in Figure 7, is a minimum at a Rb/(Rb + Na) ratio of 0.71 and 0.72 respectively. Within experimental error, the composition having the minimum relaxation time coincides with that predicted on the basis of the slowest moving ion.

C. Correlation between Diffusion Coefficient and Internal Friction Peak Height

As mentioned previously, the magnitude of an internal friction peak depends upon the concentration of "active" units, the relaxation strength of the units, and the distribution of relaxation times. Condensing this into equation form yields:

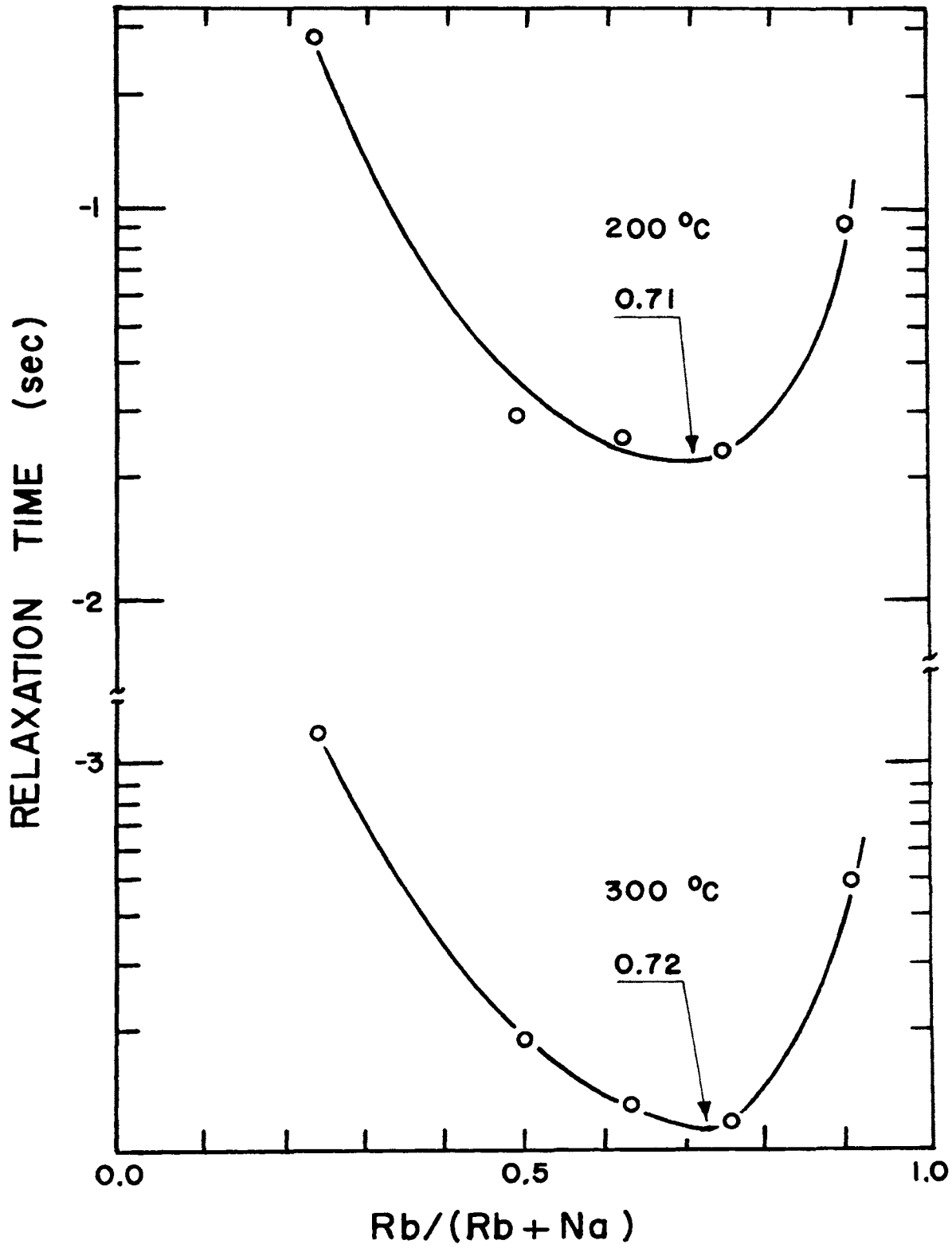

Figure 7. Change in Relaxation Time for the Mixed Alkali Internal Friction Peak in (1 - X) $Na_2O \cdot X\ Rb_2O \cdot 3\ SiO_2$ Glasses

$$Q^{-1} \propto [C \cdot P][W][\delta] \tag{7}$$

C•P = Concentration of active units
C = Total concentration of units
P = Probability that a unit is active

W = Relaxation strength

δ = A factor related to the distribution of relaxation times

For the Na - Rb system, the distribution of relaxation times and hence $[\delta]$, remains constant, Table V. For a given relaxation process $[W]$ should not change significantly with composition and is, therefore, assumed constant. Assuming purely statistical pairing, C = 2 Nna (1 - Nna). The probability of a relaxing unit being active, P, is considered proportional to the mobility of the unit; a sodium-rubidium ion pair in this example. As previously shown in Figures 6 and 7, the mobility of a sodium-rubidium ion pair is dependent upon the diffusion coefficient of the slowest moving ion, D_{slow}. Therefore, equation 7 can be rewritten as:

$$Q^{-1} \propto [\text{Constant}_1][2\ \text{Nna}\ (1 - \text{Nna}) \cdot D_{slow}] \tag{8}$$

In the Na - Rb glasses the change in D_{slow} is much greater than the change in Nna (1 - Nna). As Nna varies from 0.25 to 0.75, D_{slow} changes by a factor of ten while C varies from only 0.38 to 0.50. Consequently the change in the diffusion coefficient, D_{slow}, determines the composition at which the peak height is a maximum, i.e., where D_{slow} is a maximum.

One example occurs in the literature which serves as a test for the predicted correlation between internal friction and diffusion. Evstrop'ev[18] measured the diffusion coefficients for both sodium and potassium in (20 - X) Na_2O•X K_2O•80 SiO_2 glasses at 415°C. Internal friction for the (25 - X) Na_2O•X K_2O•75 SiO_2 glasses has been measured

by Shelby.[8] Although the composition of these two glass systems is slightly different, a general comparison is still possible.

The diffusion coefficient curves for sodium and potassium intersect at a K/(K + Na) ratio of 0.77. According to the results of this study the maximum height of the mixed alkali internal friction peak should occur at this composition. Shelby's data show that the maximum mixed peak height is at a K/(K + Na) ratio of 0.60. The exact effect of the compositional difference of these two systems on diffusion and internal friction is unknown and the difference in ion ratios is presently attributed to the difference in composition. However, there seems to be basic agreement in the Na - K glasses as well as the Na - Rb glasses.

Equation 8 is also useful in understanding why the height of the mixed alkali peak varies between various mixed alkali compositional systems. At a constant ion ratio equation 8 becomes:

$$Q^{-1} \propto \left[\text{Constant}_2\right]\left[D_{slow}\right] \qquad (9)$$

Therefore for comparable compositions, systems in which D_{slow} is greatest should have the largest mixed peak. At 415°C, the slowest moving ion, potassium, in a 10 Na_2O·10 K_2O·80 SiO_2 glass has a diffusion coefficient, D_K, of 2.2×10^{-10} cm^2/sec[18]. At the same temperature for a 12.5 Na_2O·12.5 Rb_2O·75 SiO_2 glass, the slowest moving ion, rubidium, has a diffusion coefficient, D_{Rb}, of 5.5×10^{-11} cm^2/sec. Ignoring for a moment the difference in total alkali content for the two glasses, equation 9 shows that the mixed alkali peak height for the Na - K glass should be higher than that for the Na - Rb glass since $D_K > D_{Rb}$. The height above background of the mixed alkali peak for a 12.5 Na_2O·12.5 K_2O·75 SiO_2 glass is 30.3[8] while for a 12.5 Na_2O·12.5 Rb_2O·75 SiO_2 glass it is 20.7. The compositional difference between the Na - K glasses in

which diffusion and internal friction were measured will not change the previous conclusion. It is logical to expect that the diffusion coefficient for potassium would be even larger in a 75 mole % SiO_2 glass than in the 80 mole % SiO_2 glass. This would make the difference in D_{slow} values between the Na - K and Na - Rb glasses even greater and the peak height prediction based on equation 9 would be the same. Therefore, the magnitude of D_{slow} is very important in determining the height of the mixed alkali peak within and between compositional systems.

In the above example no allowance was made for any variation in W. Caution must be exercised, however, as the exact variation of W is not known. Shelby[8] assumed it to vary with radius ratio of the alkali ions but to remain constant within a system. Using Goldschmidt radii $K^+/Na^+ = 1.36$ and $Rb^+/Na^+ = 1.52$, the ratio varies by only 10%. Although equation 7 has limitations, it shows a relationship between the mixed alkali peak and the alkali ion diffusion coefficients.

The height of the alkali peak is also closely associated with the appropriate diffusion coefficient. In Figure 8 the alkali peak height changes significantly with the Al/Na ratio. With increasing Al/Na ratio, the alkali peak height first decreases, and then increases to a maximum at Al/Na = 1; after which, it decreases again. The sodium diffusion coefficient varies with Al/Na ratio in precisely the same manner, as shown by Figure 9. Although the compositions are not exactly the same, the relationship between the height of the alkali peak and the diffusion coefficient is illustrated. That is, the changes in the sodium ion diffusion coefficient (constant temperature) correlate very well with the changes in the alkali peak height. In the sodium aluminosilicate glasses with Al/Na = 1 the height of the alkali peak

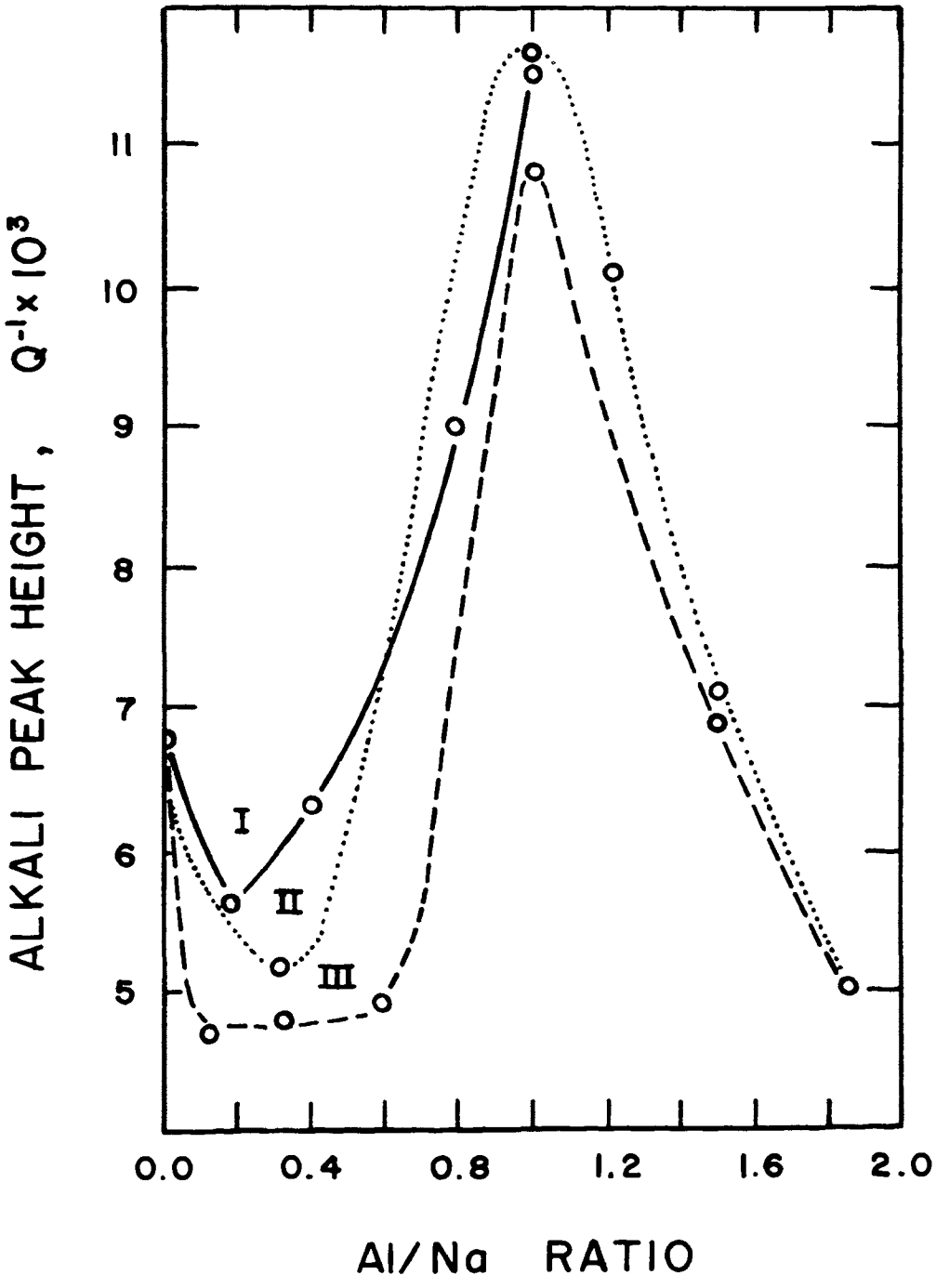

Figure 8. Alkali Peak Height for Sodium Aluminosilicate Glasses.[22] I = $Na_2O \cdot X\ Al_2O_3 \cdot (3 - X)SiO_2$, II = $(2 - X)Na_2O \cdot X\ Al_2O_3 \cdot (6 - 2X)SiO_2$, III = $(2 - X)\ Na_2O \cdot X\ Al_2O_3 \cdot 6SiO_2$

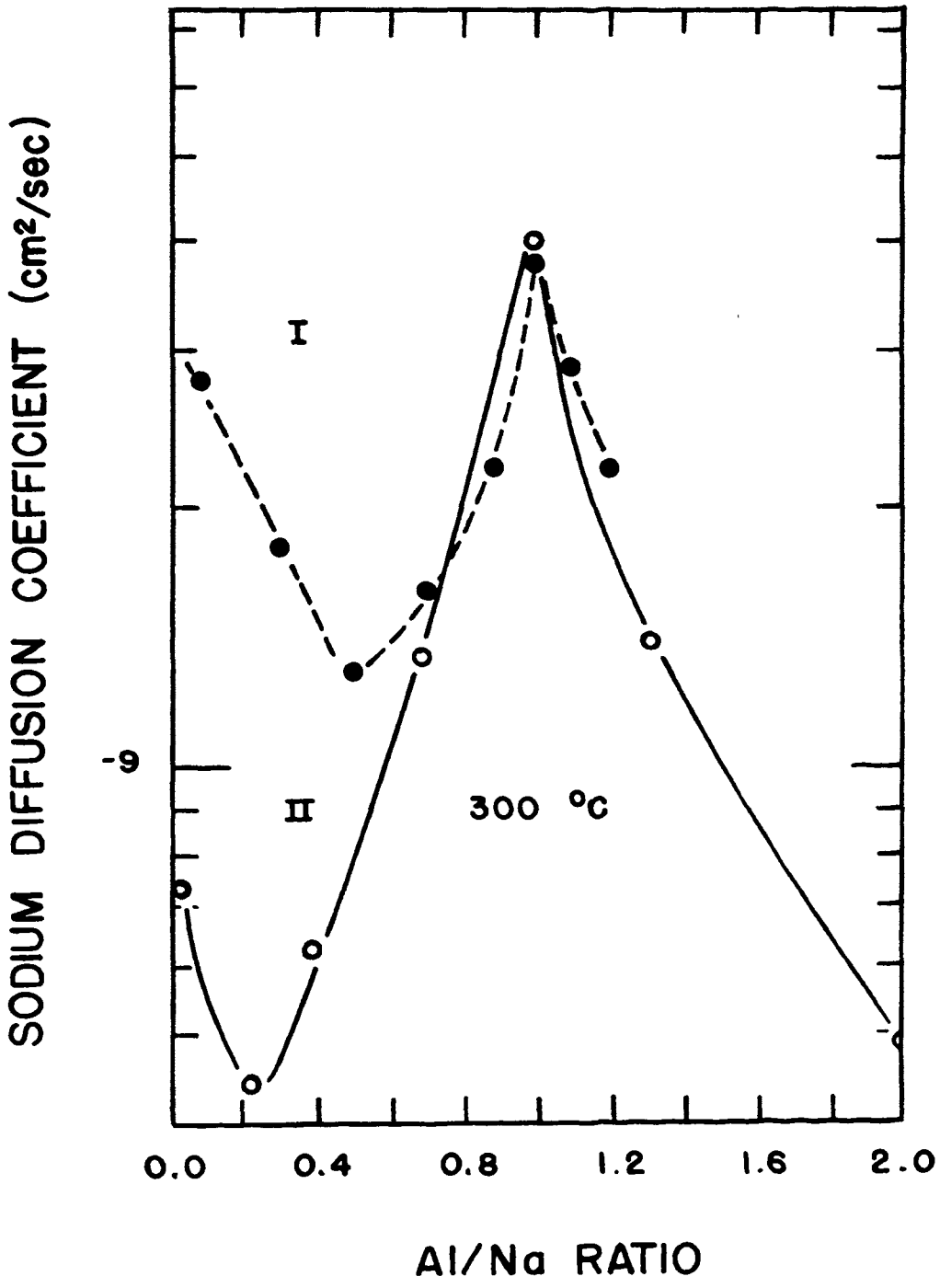

Figure 9. Self Diffusion Coefficients for Sodium in Sodium Aluminosilicate Glasses. I = $Na_2O \cdot X\ Al_2O_3 \cdot 2\ SiO_2$ [23], II = $13\ Na_2O \cdot X\ Al_2O_3 \cdot (87 - X)\ SiO_2$ [24]

remains almost constant even though the Na_2O concentration varies from 25 to 12.5 mole percent. These glasses also have nearly the same value for the sodium diffusion coefficients, Figure 9.

A summary of existing diffusion and corresponding alkali peak height data is given in Table VI. Within a compositional system, the height of the alkali peak varies in the same manner as the diffusion coefficient. The relationship between diffusion coefficient and peak height also applies between alkali systems. For example, for X = 0.25, the alkali peak heights for silicate glasses increase in the order Rb, K, and Na. The diffusion coefficients also increase in the same order. The height of the alkali peak is obviously sensitive to changes in the alkali ion diffusion coefficient.

TABLE VI

Alkali Peak Height and Diffusion Coefficients for Various Silicate and Germanate Glasses

X $Na_2O \cdot (1-X)\ GeO_2$	Alkali Peak Height [19]	D_{Na} [20] $(\frac{cm^2}{sec})$ - 400°C
X = 0.05	3.5×10^{-3}	6.0×10^{-11}
X = 0.15	3.5×10^{-3}	6.9×10^{-11}
X = 0.25	4.9×10^{-3}	1.1×10^{-9}
X = 0.30	5.7×10^{-3}	6.3×10^{-9}
X $Na_2O \cdot (1-X)\ SiO_2$	Alkali Peak Height	D_{Na} [18] $(\frac{cm^2}{sec})$ - 415°C
X = 0.10	--	2.3×10^{-9}
X = 0.13	--	3.3×10^{-9}
X = 0.15	2.3×10^{-3} [6]	--
X = 0.17	3.0×10^{-3} [2]	--
X = 0.195	3.2×10^{-3} [5]	--
X = 0.20	3.5×10^{-3} [6]	5.9×10^{-9}
X = 0.25	6.7×10^{-3} [21]	9.5×10^{-9}
X = 0.30	--	1.7×10^{-8}

TABLE VI (continued)

X $K_2O \cdot (1-X)\ SiO_2$	Alkali Peak Height	D_K (18) $(\frac{cm^2}{sec})$ - 415°C
X = 0.13	--	2.4×10^{-10}
X = 0.20	--	6.5×10^{-10}
X = 0.25	4.7×10^{-3} (21)	1.4×10^{-9}
X $Rb_2O \cdot (1-X)\ SiO_2$	Alkali Peak Height	D_{Rb} $(\frac{cm^2}{sec})$ - 415°C
X = 0.25	3.9×10^{-3} (21)	8.7×10^{-10}

V. CONCLUSIONS

A correlation was found between the diffusion coefficients for sodium and rubidium ions and the mixed alkali internal friction peak for $(1 - X)\ Na_2O \cdot X\ Rb_2O \cdot 3\ SiO_2$ glasses. The maximum height for the mixed alkali peak was observed at that composition where the diffusion coefficients for the sodium and rubidium ions are equal. The mechanism responsible for the mixed alkali peak is considered to be a cooperative rearrangement of the sodium-rubidium ions. The slowest moving ion is the rate controlling factor for this rearrangement.

The internal friction for the Na - Rb silicate glasses is very similar to that for other mixed alkali silicate systems. Therefore, the conclusions drawn for the Na - Rb glasses should apply in general to other mixed alkali silicate glasses.

The height (magnitude) of the alkali peak, as well as the mixed alkali peak, is closely associated with the alkali ion diffusion coefficients. An increase in the alkali ion diffusion coefficient, due to compositional changes, is associated with a corresponding increase in magnitude for the alkali peak. A change in height for the alkali internal friction peak is sufficiently indicative of a corresponding change in the diffusion coefficient that measurements of an internal friction peak can be used to evaluate whether the alkali diffusion coefficient is increasing or decreasing as the composition is varied.

VI. APPENDICES

APPENDIX A

SAMPLE PREPARATION AND HEAT TREATMENT

1. Glass Preparation and Melting

Glasses of the general composition (1 - X) Na_2O·X Rb_2O·3 SiO_2 were prepared from reagent grade Na_2CO_3, Rb_2CO_3 and potter's flint (99.98% SiO_2). The batch materials were mixed by adding enough acetone to make a slurry and stirring until nearly dry. The batch was placed in a dryer overnight for final drying.

Due to the high viscosity of the melt, 0.03 wt. % NaI was added to promote fining. The platinum crucible was preheated to 1500°C and small charges were made, allowing enough time for fining between charges. The remainder of the batch was kept in the dryer between charges to minimize water absorption. Prior to each charge the melt was stirred with a fused silica rod to assure homogeneity.

2. Sample Forming and Heat Treatment

Rectangular bars 2/3" x 1/2" x 6" and 1/4" x 1/2" x 6" were made by pouring the bubble-free melt into stainless steel molds preheated to approximately 200°C. The bars were quickly removed from the molds and placed in a preheated furnace where they were held at their annealing temperature, see Table I, for four hours and slowly cooled to room temperature. Fibers approximately 0.5 mm in diameter were pulled from the same melt, annealed at the appropriate temperature for thirty minutes, and slowly cooled to room temperature.

APPENDIX B

INTERNAL FRICTION

1. Inverted Torsion Pendulum

The apparatus shown in Figure 10, and the technique have been described elsewhere.[8, 25] Briefly, internal friction was measured as a function of temperature at frequencies from 0.05 to 1.00 Hz. The frequency was varied by using fibers of different size and by adjusting the movable weights on the horizontal inertia arm. A light beam was reflected from a mirror on the oscillating pendulum and focused on a solar cell faced by two parallel slits. The time necessary for the light beam to travel the fixed distance between the slits is inversely proportional to the amplitude of vibration. The internal friction was calculated from equation 2 by setting the amplitude ratio equal to t_n/t_o, where t_n equals the time required for the light beam to pass between the slits on the n^{th} cycle and t_o on the zeroth cycle.

2. Resonance Technique Based on Forster's Method

This apparatus, Figure 11, and technique have been described previously.[26, 27] The frequency was varied by changing the physical size of the bar, usually shortening it. The specimen was driven at its resonant frequency and allowed to decay, thus permitting the number of attenuated wave cycles occurring between known amplitude limits to be determined. Internal friction was calculated from equation 2 by setting the amplitude ratio equal to A_U/A_L, where A_U equals the upper amplitude limit and A_L the lower amplitude limit.

3. Data

A summary of the internal friction data is given in Table VII.

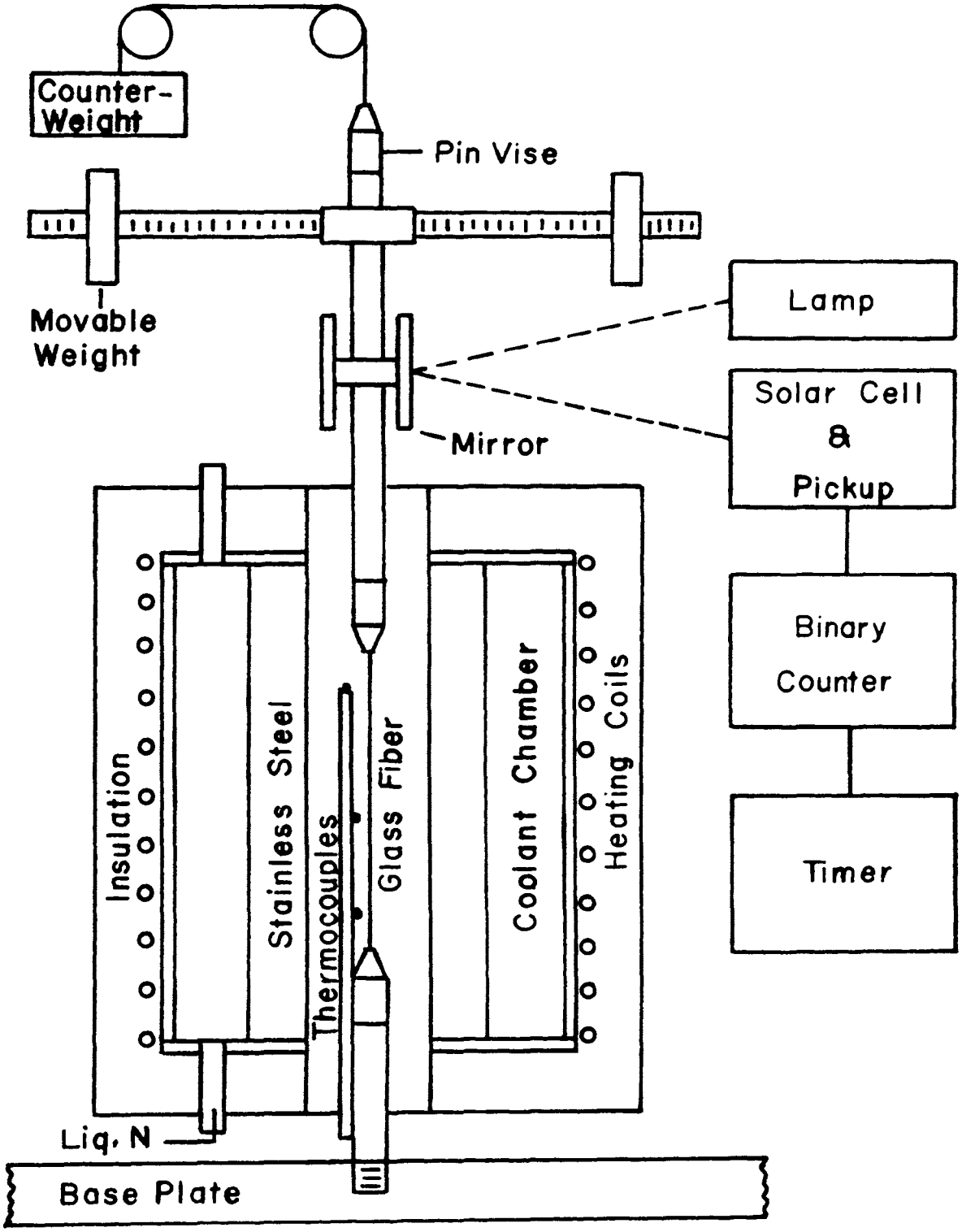

Figure 10. Inverted Torsion Pendulum and Furnace

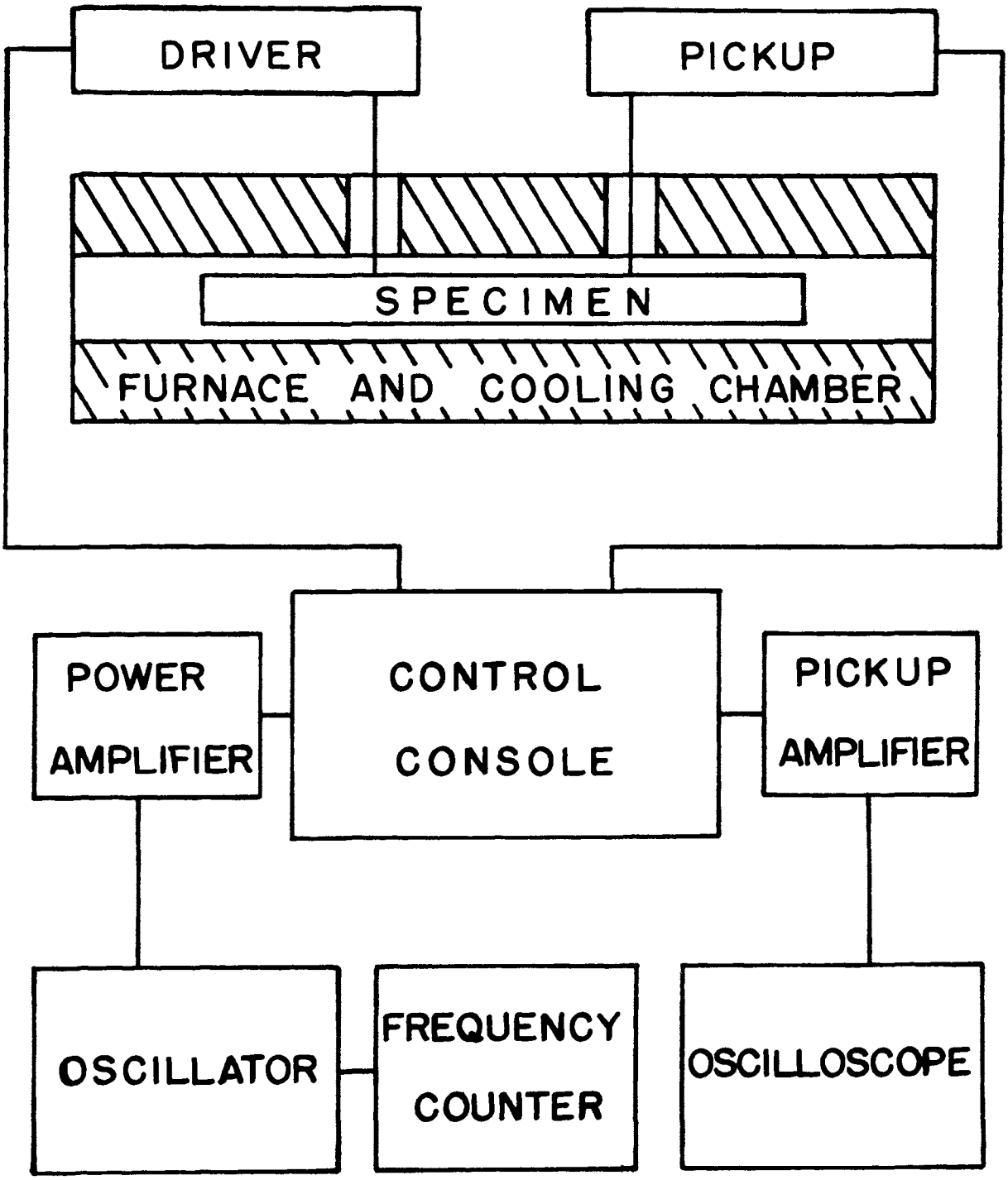

Figure 11. Sonic Apparatus and Furnace

TABLE VII

Mixed Peak Temperature, Height Above Background, and Frequency

Glass No.	Mixed Peak Temp. (°C)	Mixed Peak Height (10^3)	Frequency (Hz)
II*	248 ± 4	3.0 ± 0.3	0.400
III*	235 ± 3	5.8 ± 0.2	0.400
IV	176 ± 2		0.113
	191 ± 2		0.315
	194 ± 2	15.0 ± 0.2	0.413
	354 ± 5		1684
	379 ± 5		2421
V	144 ± 2		0.117
	160 ± 2		0.372
	162 ± 2	21.3 ± 0.2	0.429
	166 ± 2		0.601
	167 ± 2		0.650
	314 ± 5		1929
	331 ± 5		2406
VI	144 ± 2		0.105
	161 ± 2	23.0 ± 0.2	0.389
	170 ± 2		0.855
	303 ± 5		1870
	327 ± 5		2782
VII	139 ± 2		0.081
	157 ± 2		0.309
	160 ± 2	22.9 ± 0.2	0.389
	294 ± 4		1007
	310 ± 5		2139
VIII	176 ± 2	17.2 ± 0.2	0.370
	181 ± 2		0.527
	338 ± 5		1641

*Data taken from Shelby[8]

Figures 12-16 show internal friction curves for each composition at a frequency of approximately 0.4 Hz. The background at intermediate temperatures was obtained by fitting a tenth order polynomial to the high and low temperature portions of the internal friction curves, where the total damping is attributed to background damping. Coefficients of the polynomial were determined by a computer program and were used to evaluate the polynomial in the intermediate temperature regions. Activation energies were evaluated by using a least squares approximation to a straight line and equation 3.

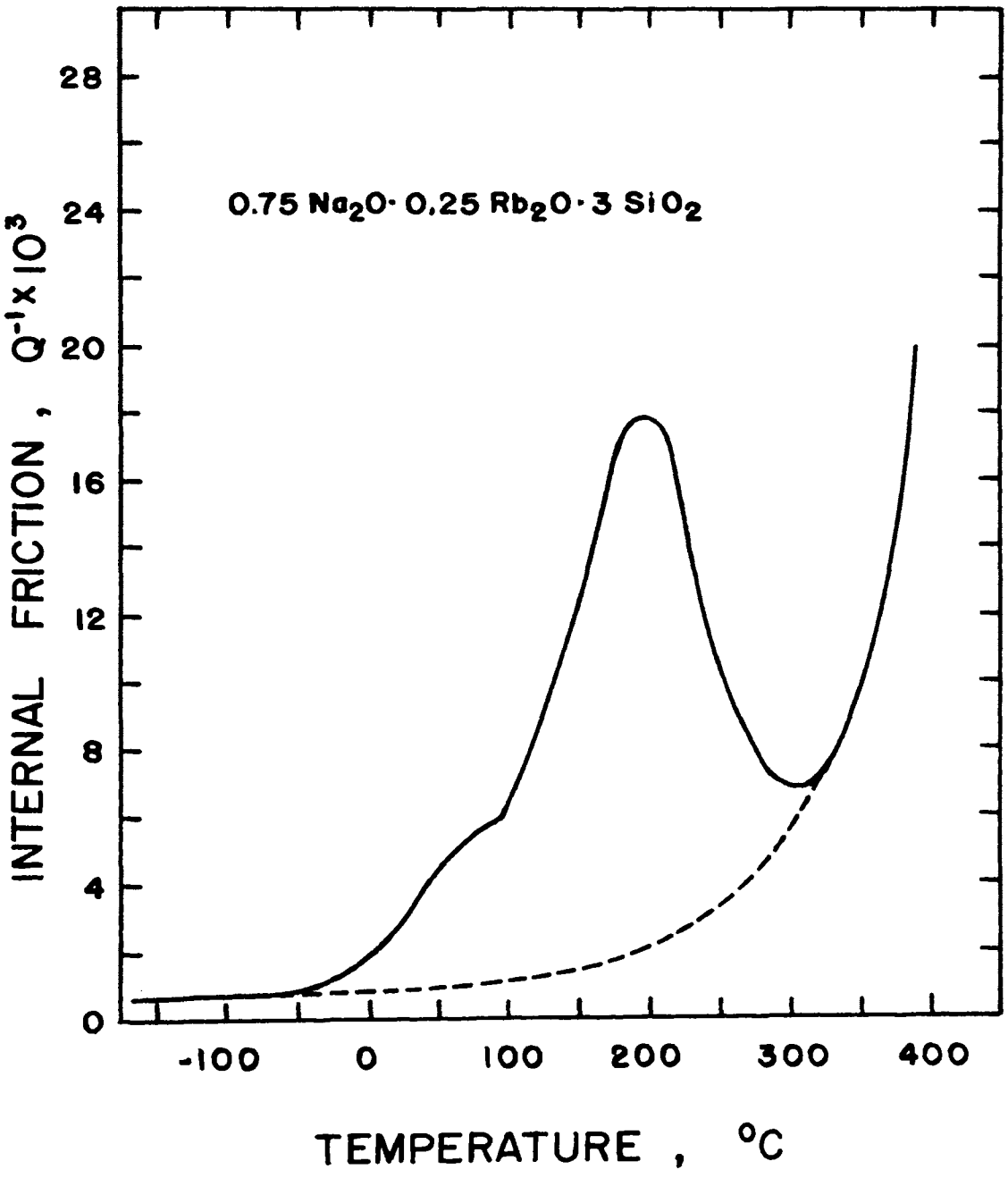

Figure 12. Internal Friction Curve for 0.75 $Na_2O \cdot 0.25\ Rb_2O \cdot 3\ SiO_2$, Freq. = 0.4 Hz

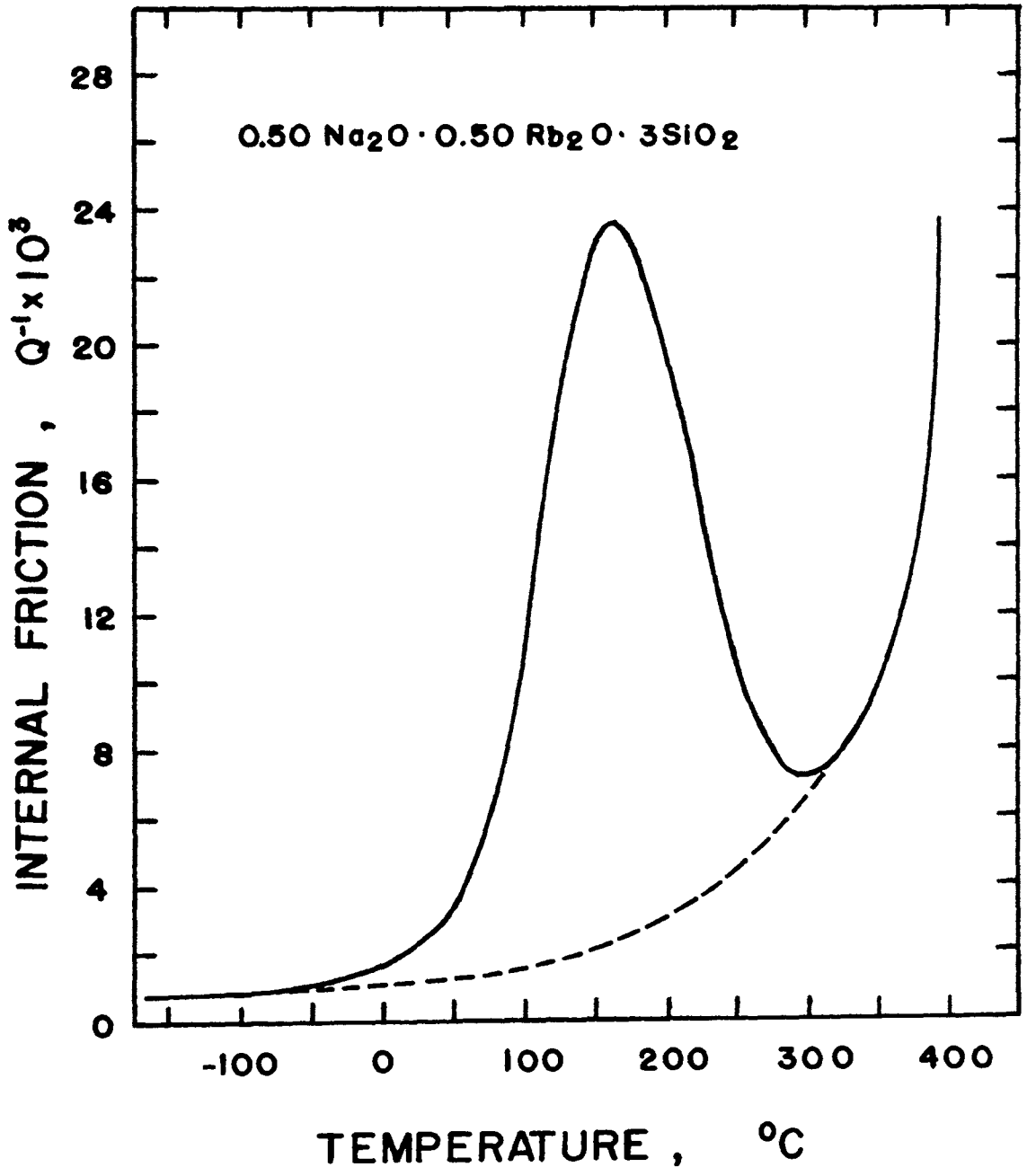

Figure 13. Internal Friction Curve for 0.50 Na_2O·0.50 Rb_2O·3 SiO_2, Freq. = 0.4 Hz

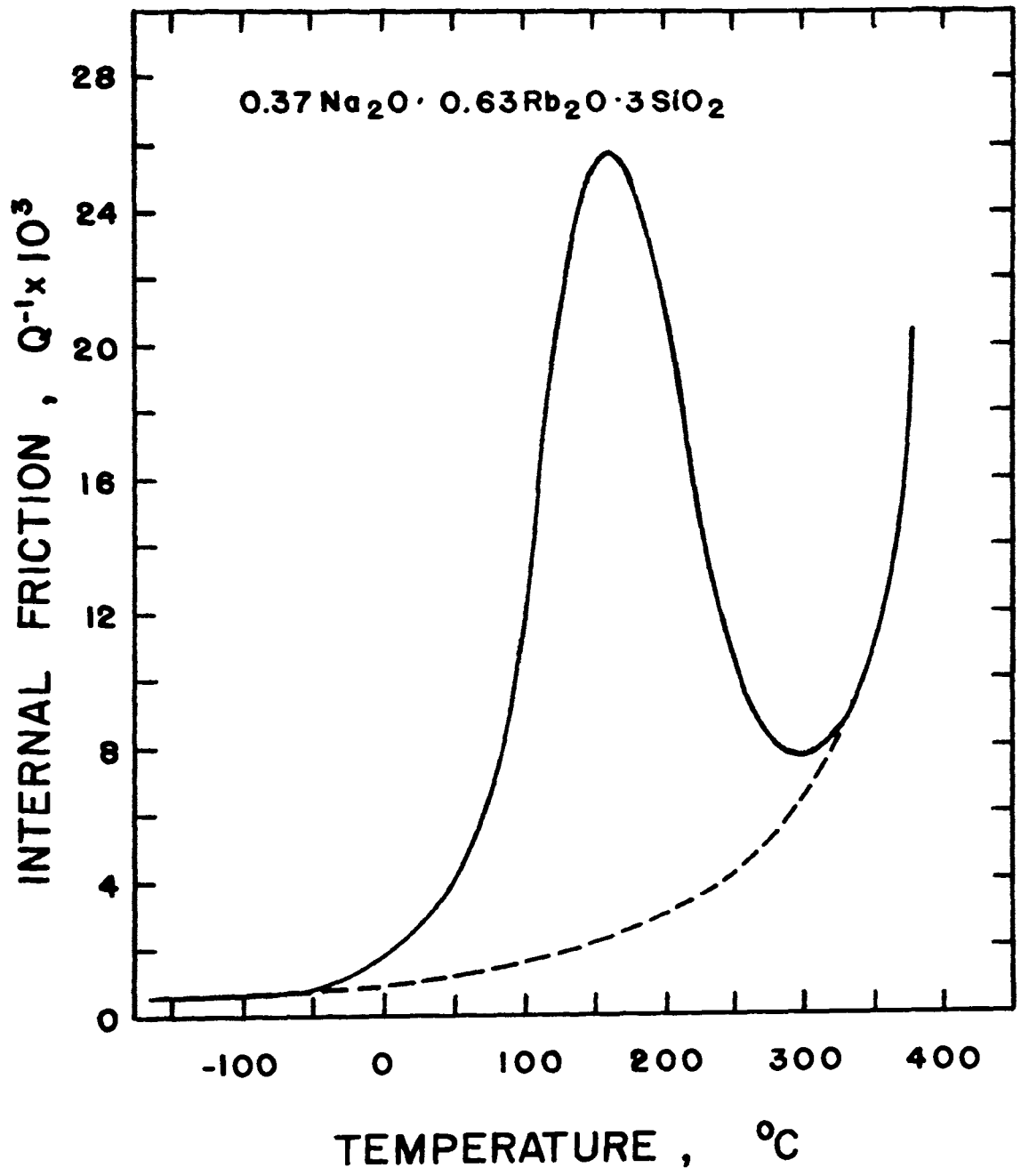

Figure 14. Internal Friction Curve for 0.37 Na_2O·0.63 Rb_2O·3 SiO_2, Freq. = 0.4 Hz

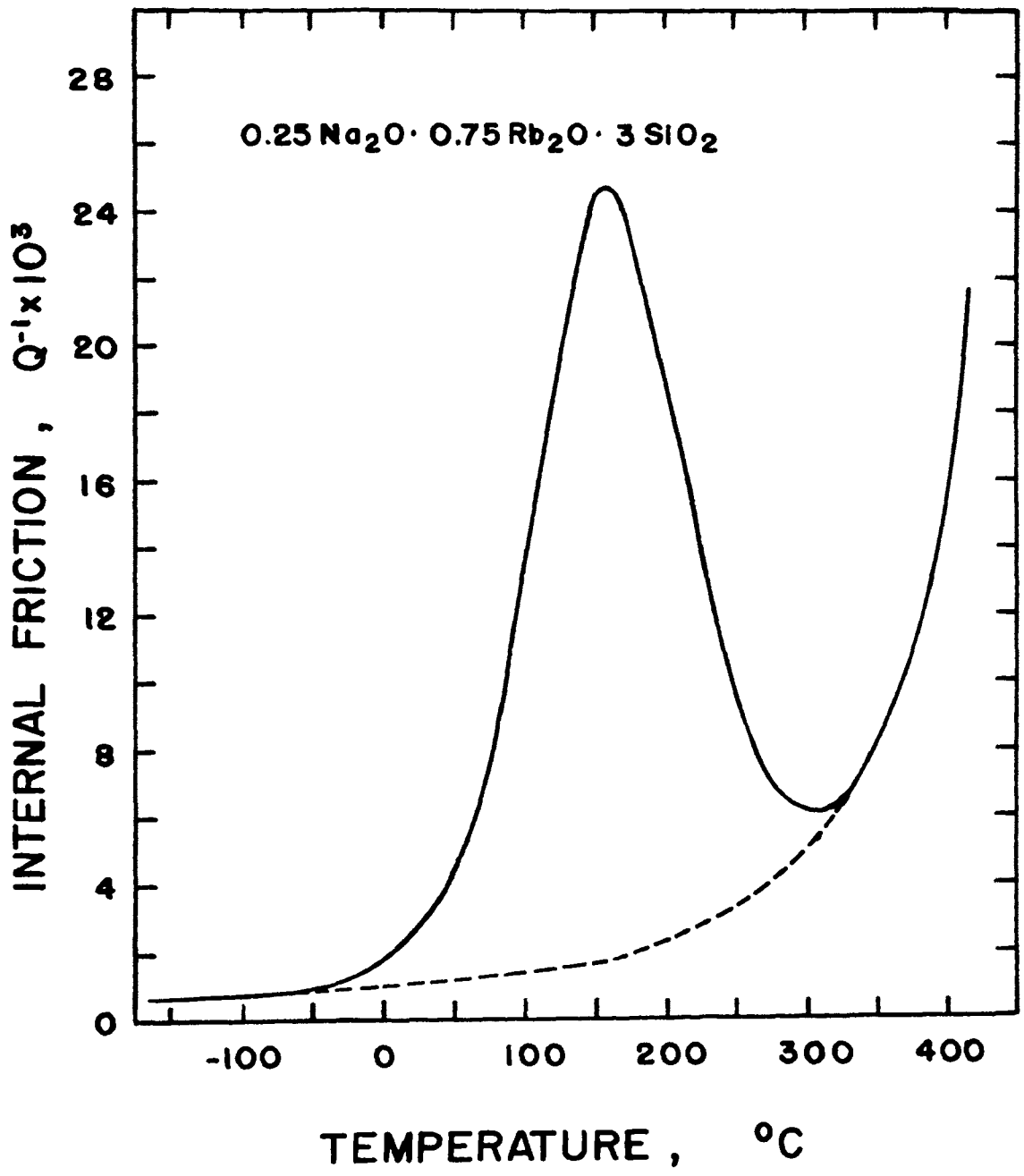

Figure 15. Internal Friction Curve for 0.25 $Na_2O \cdot 0.75\ Rb_2O \cdot 3\ SiO_2$, Freq. = 0.4 Hz

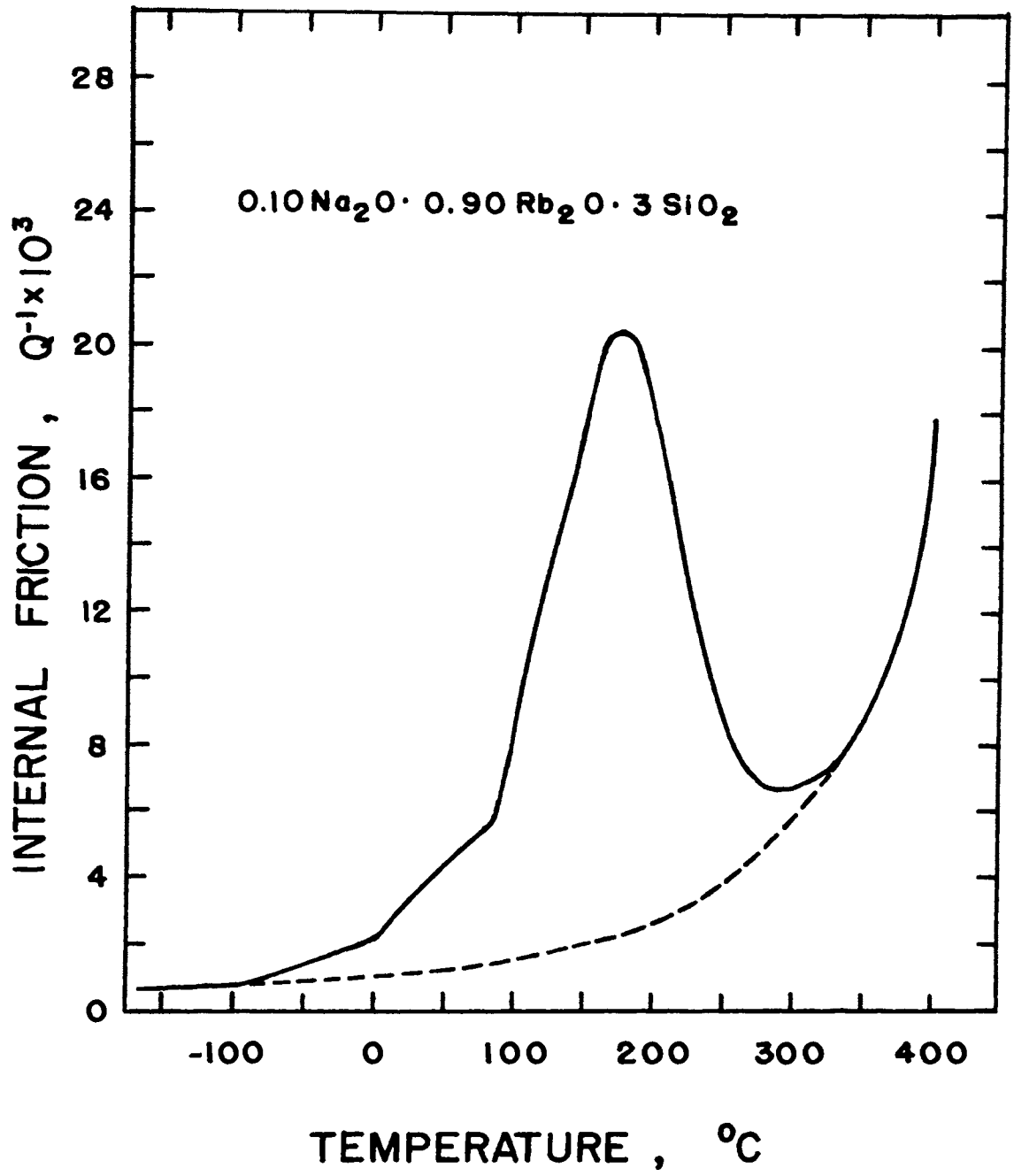

Figure 16. Internal Friction Curve for 0.10 $Na_2O \cdot 0.90\ Rb_2O \cdot 3\ SiO_2$, Freq. = 0.4 Hz

APPENDIX C

DIFFUSION

1. Technique and Equipment

The self diffusion coefficients of sodium and rubidium ions were determined by using a radioactive tracer and thin-sectioning technique, Figure 17. Samples were cut from the annealed bar with a diamond saw using oil as a coolant. The samples were wiped free of oil, using acetone, and stored in a desiccator. The faces of each sample were polished on the same apparatus used for sectioning. This apparatus has been described previously.[11] After polishing, the desired isotope was vapor deposited on one face in a vacuum evaporator. The coated samples were heat treated in an electrically heated tube furnace. The furnace was probed with a thermocouple to determine the zone with the lowest temperature gradients. A four-inch zone was found in which the temperature variation never exceeded $1/2^{\circ}C$. After the furnace reached the desired temperature, two plated samples were placed on a stainless steel block and positioned in the nearly constant temperature zone. The temperature was determined from a Chromel-Alumel thermocouple (calibrated by the National Bureau of Standards) in contact with the metal block. After being at temperature for the desired length of time, the samples were removed from the furnace and cooled in air. Surface diffusion effects were eliminated by partially removing the edges of the samples on a lapping wheel. The samples were then mounted and sectioned. The activity of each removed section was determined by a scintillation counter. Sections were removed until the measured activity reached approximately three times the background. The remaining sample was weighed after each section with a balance capable of

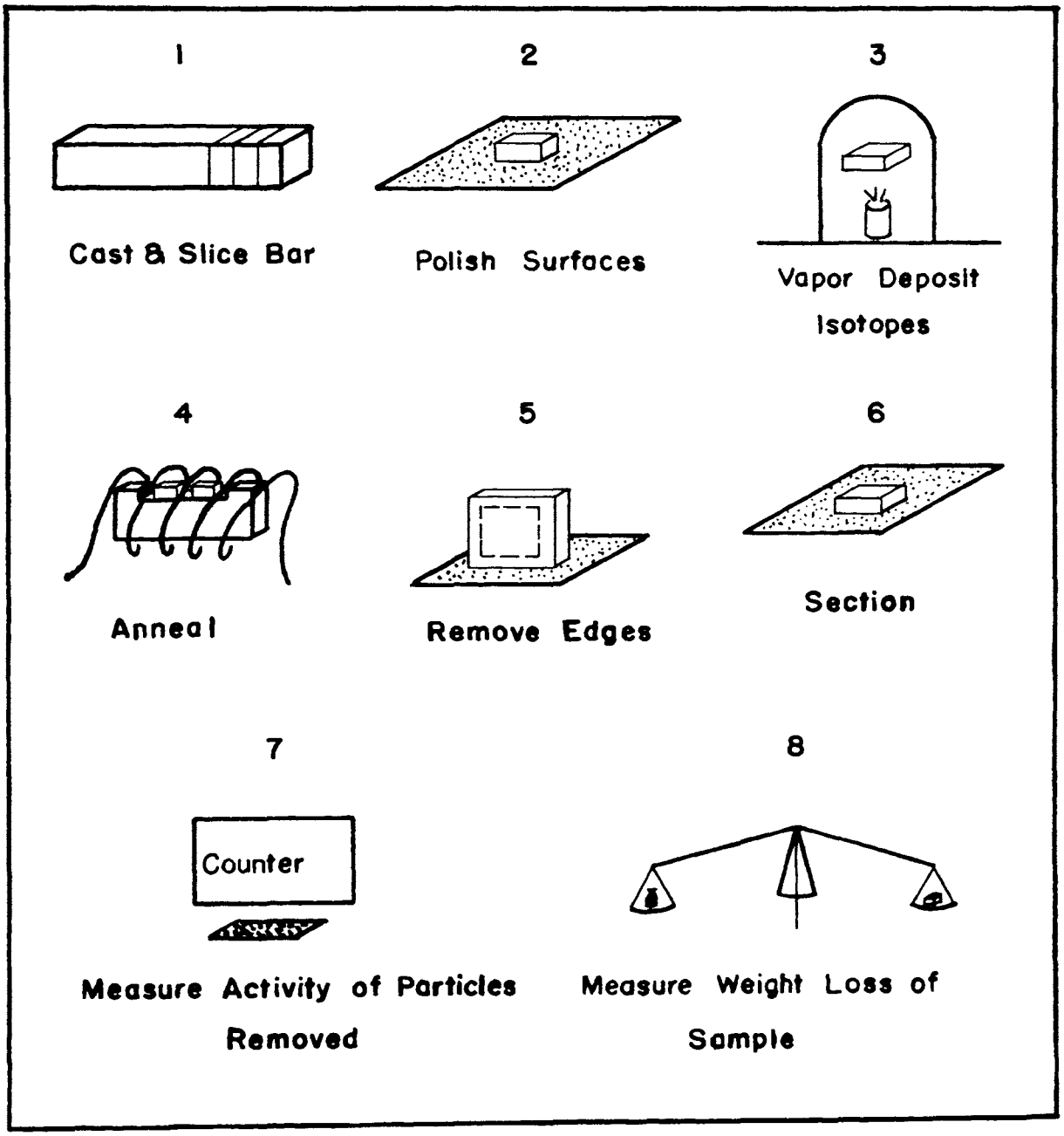

Figure 17. Procedure for Diffusion Measurements

reading to 10^{-5} gm. Cross-sectional areas of the samples were determined from the product of average measurements made with a micrometer. The density of the samples was measured by the liquid emersion technique.

2. Data

The experimentally determined values for the self diffusion coefficients of sodium and rubidium ions at various temperatures are given in Table VIII. These values were obtained by taking the average value of two samples which were processed simultaneously. The difference between the two simultaneously measured diffusion coefficients never exceeded ten percent. The least squares technique was used to determine the best straight line fit to the data. Activation energies were calculated from the slope of the straight lines.

TABLE VIII

Experimental Data for the Self Diffusion Coefficients of Sodium and Rubidium Ions

Glass No.	Diffusion Coefficient ($\frac{cm^2}{sec}$) D_{Na}	Diffusion Coefficient ($\frac{cm^2}{sec}$) D_{Rb}	Temp. (°C) (± 1/2°C)
I	3.63×10^{-9}	--	359
	1.08×10^{-8}	--	404
	1.90×10^{-8}	--	438
	4.52×10^{-8}	--	479
	--	4.54×10^{-12}	389
	--	1.08×10^{-11}	431
	--	3.08×10^{-11}	462
	--	9.41×10^{-11}	491
IV	5.65×10^{-10}	--	366
	1.49×10^{-9}	--	402
	5.41×10^{-9}	--	447
	1.42×10^{-8}	--	477
	--	5.55×10^{-12}	380
	--	1.12×10^{-11}	404
	--	7.25×10^{-11}	451
	--	4.33×10^{-10}	495
V	1.07×10^{-10}	--	367
	3.45×10^{-10}	--	406
	1.68×10^{-9}	--	459
	8.92×10^{-9}	--	512
	--	2.09×10^{-11}	387
	--	4.65×10^{-11}	415
	--	2.70×10^{-10}	458
	--	1.48×10^{-9}	507
VII	4.75×10^{-11}	--	377
	1.23×10^{-10}	--	407
	3.55×10^{-10}	--	440
	1.46×10^{-9}	--	478
	--	6.05×10^{-11}	378
	--	1.68×10^{-10}	409
	--	5.02×10^{-10}	450
	--	3.00×10^{-9}	495

TABLE VIII (Continued)

Glass No.	Diffusion Coefficient ($\frac{cm^2}{sec}$) D_{Na}	Diffusion Coefficient ($\frac{cm^2}{sec}$) D_{Rb}	Temp. (°C) (± 1/2°C)
IX	2.19×10^{-11}	--	387
	8.20×10^{-11}	--	418
	2.25×10^{-10}	--	449
	1.26×10^{-9}	--	506
	--	3.00×10^{-10}	380
	--	1.12×10^{-9}	417
	--	1.76×10^{-9}	441
	--	6.43×10^{-9}	504

VII. BIBLIOGRAPHY

1. Fitzgerald, J. V., "Anelasticity of Glass: II, Internal Friction and Sodium Ion Diffusion in Tank Plate Glass, a Typical Soda-Lime-Silica Glass", Jour. Amer. Cer. Soc. 34 (11) 339-344 (1951).

2. Forry, K. E., "Two Peaks in the Internal Friction as a Function of Temperature in Some Soda Silicate Glasses", Jour. Amer. Cer. Soc. 40 (2) 90-94 (1957).

3. Hoffman, L. C. and Weyl, W. A., "A Survey of the Effect of Composition on the Internal Friction of Glass", Glass Industry 38 (2) 81-85 (1957).

4. Deeg, E., "Relationship between Structure and Mechanical-Acoustical Properties of Single Silicate Glasses, IV", Glastechn. Ber. 31 (6) 229-240 (1958).

5. Rotger, H., "Elastic Relaxation Behavior of Single and Mixed-Alkali Silicates and Borates", Glastechn. Ber. 31 (2) 54-60 (1958).

6. Jagdt, R., "Studies of Relaxation Phenomena in Alkali Silicate Glasses", Glastechn. Ber. 33 (1) 10-19 (1960).

7. Steinkamp, W. E., Shelby, J. E., and Day, D. E., "Internal Friction of Mixed-Alkali Silicate Glasses", Jour. Amer. Cer. Soc. 50 (5) 271 (1967).

8. Shelby, J. E., "Internal Friction of Mixed-Alkali Silicate Glasses", Ph.D. Thesis, The University of Missouri-Rolla, (1967).

9. de Waal, H., "Internal Friction of Sodium Disilicate Glass after Ion Exchange", P. Chem. Glass 10 (3) 108-116 (1969).

10. Forster, F., "New Method for Determination of Modulus of Elasticity and Damping", Z. Metalk. 29 (4) 109-115 (1937).

11. Williams, E. L., and Heckman, R. W., "Sodium Diffusion in Soda-Lime-Aluminosilicate Glasses", P. Chem. Glass 5 (6) 166-171 (1964).

12. Zener, C., "Stress Induced Preferential Orientation of Pairs of Solute Atoms in Metallic Solid Solution", Phys. Rev. 71 (1) 34-38 (1947).

13. Hino, J., Tomizuka, C., and Wert, C., "Internal Friction and Diffusion in 31% Alpha Brass", Acta Met. 5 41-49 (1957).

14. Steinkamp, W. E., Unpublished Data (1967).

15. de Waal. H., "On the Internal Friction in Ion-Exchanged Sodium Silicate Glasses and in Sodium Aluminoborate Glasses", Ph.D. Thesis, Technical High School Delft, (1961).

VII. BIBLIOGRAPHY (continued)

16. Nowick, A. S., "Anelastic Phenomena in Metals and Nonmetallics", Internal Friction, Damping, and Cyclic Plasticity, ASTM STP 378 (1964).

17. Reed-Hill, R. E., Physical Metallurgy Principles, Van Nostrand, p. 299 (1964).

18. Evstrop'ev, K. K., "Study of the Diffusion of Certain Alkali-Metal Ions in Silicate Glasses with the Aid of Radioactive Isotopes", Structure of Glass, Vol. 2, Consultants Bureau, 237-240 (1959).

19. Shelby, J. E., Unpublished Data (1969).

20. Evstrop'ev, K. K., and Pavlovskii, V. K., "Microstructure of One-Alkali and Two-Alkali Germanate Glasses", Structure of Glass, Vol. 3, Consultants Bureau, 103-105 (1963).

21. Shelby, J. E., and Day, D. E., "Mechanical Relaxations in Mixed-Alkali Silicate Glasses: I, Results", Jour. Amer. Cer. Soc. 52 (4) 169-174 (1969).

22. Day, D. E., "The Internal Friction of Soda Aluminosilicate Glasses and Its Structural Interpretation", Ph.D. Thesis, The Pennsylvania State University, p. 72 (1961).

23. Terai, R., "Self-Diffusion of Sodium Ions and Electrical Conductivity in Sodium Aluminosilicate Glasses", P. Chem. Glass 10 (4) 146-152 (1969).

24. Tsekhomskii, V. A., Mazurin, O. V., and Evstrop'ev, K. K., "Nature of the Conductivity of Aluminosilicate Glasses", Soviet Physics-Solid State 5 (2) 426-428 (1963).

25. Miller, T. F., "Construction and Calibration of an Inverted Torsion Pendulum for Measuring the Internal Friction of Glass", M. S. Thesis, The University of Missouri-Rolla, (1965).

26. Wachtman Jr., J. B., and Tefft, W. E., "Effect of Suspension Position on Apparent Values of Internal Friction Determined by Forster's Method", The Review of Scientific Instruments 29 (6) 517-520 (1958).

27. Taylor, S. W., "Internal Friction of Phase Separated Glasses", M. S. Thesis, The University of Missouri-Rolla, (1969).

VIII. VITA

Gary Lee McVay was born on January 23, 1943, in Hawthorne, California. He received his primary education in Springfield, Missouri, and his secondary education in St. Charles, Missouri. He has received his college education from the University of Missouri - Rolla, in Rolla, Missouri. He received a Bachelor of Science degree in Metallurgical Engineering in May 1966 and a Master of Science degree in Ceramic Engineering in May 1968.

He has been enrolled in the Graduate School of the University of Missouri - Rolla since January 1966 and has held the NSF Traineeship for the period September 1966 to August 1968 and the NASA Traineeship for the period September 1968 to the present time.